Polymerisation of ethylene or propylene with heterogeneous metallocene catalysts on clay minerals

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Abstract

Heterogeneous metallocene catalysts avoid reactor fouling in olefin polymerisations. For technical use the metallocene catalysts must be fixed on carriers. Silica is one of the favoured inorganic carriers. But the activities of heterogeneous metallocene catalysts on silica in ethylene and propylene polymerisation are often lower than those of comparable homogeneous catalyst systems.

We tested the clay minerals kaolin and montmorillonite as inorganic carriers for the polymerisation of ethylene and propylene with commercially available titanocenes and zirconocenes and also with new types of titanocenes.

The heterogeneous catalysts on kaolin were less active in ethylene polymerisation as comparable homogeneous catalysts and they were not active in propylene polymerisation. In contrast the heterogeneous catalysts on montmorillonite are often more active in ethylene or propylene polymerisation than comparable homogeneous systems. As cocatalysts trimethylaluminium ($AlMe_3$, TMA) and triisobutylaluminium ($Al(^iBu_3)$, TIBA) were used for heterogeneous polymerisations. As catalysts commercially available titanocenes and zirconocenes and also four titanocenes with unusual structures were tested which Lang et al. had synthesised.

The high activities in ethylene or propylene polymerisations with montmorillonite may be due to the special structure of the montmorillonite carrier. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous Ti and Zr metallocenes; Clay minerals; Montmorillonite structure

1. Introduction

Some years ago we started with homogeneous ethylene and propylene polymerisations with Ti, Zr and Hf metallocenes as catalysts [1,2].

Our experience on heterogeneous metathesis catalysis [3,4] encouraged us to start 1998 with syntheses of heterogeneous metallocene catalysts. Many publications existed at this time on heterogeneous metallocene catalysts. Most of them used silica as inorganic carrier, therefore we tested the clay minerals kaolin and montmorillonite as inorganic carriers.

In 1999 we published our first results on ethylene and propylene polymerisation with heterogeneous Ziegler–Natta and metallocene catalysts on the clay mineral montmorillonite [5].

The heterogeneous catalysts were formed in two simple reaction steps. In the first reaction an aluminium alkyl, triisobutylaluminium ($Al(^iBu_3)$, TIBA) or trimethylaluminium ($AlMe_3$, TMA) and was added

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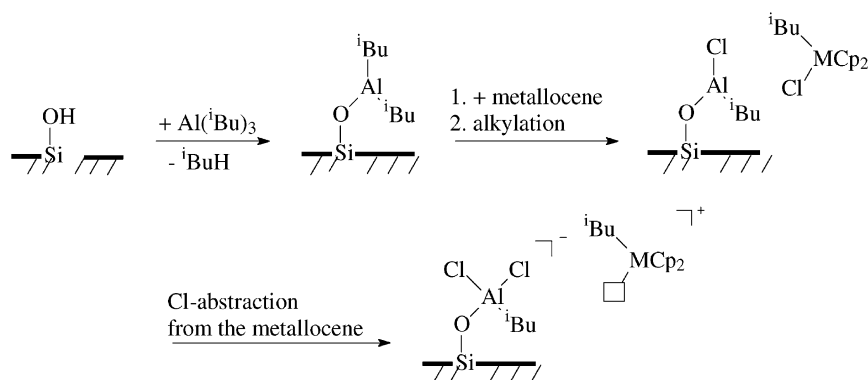heinrich.lang@uni-chemnitz.de (H. Lang).

Fig. 1. Formation of heterogeneous Ti and Zr metallocene catalysts.

to a suspension of the dried inorganic carrier. The acid Si–OH groups on the surface of the montmorillonite or kaolin react with the Lewis acid to produce a heterogeneous cocatalyst. In a second reaction step the Ti or Zr metallocene was added to the suspension and the active heterogeneous catalyst system for the ethylene or propylene polymerisation was formed. Fig. 1 presents a postulated reaction pathway. As an inorganic carrier we used kaolin, a two-layered clay mineral and montmorillonite, a three-layered clay mineral.

As catalysts we used commercially available metallocene catalysts like titanocenedichloride and zirconocenedichloride, or the Brintzinger catalyst, a bridged rac-Et(Ind)$_2$ZrCl$_2$, for olefin polymerisations.

After our first results we recognised that we were not the first to use clay minerals as inorganic carrier for metallocene catalysts for olefin polymerisation. Suga et al. had studied a variety of clay minerals as inorganic carrier [6]. In contrast to them we used predominantly the cheap and easier to handle TIBA as cocatalyst and no additional TMA.

2. Experimental

2.1. Syntheses of the titanocenes 1–4 (by Lang et al.)

(a) Synthesis of (η^5-C$_5$H$_5$)[η^5-C$_5$H$_4$SiMe$_2$CH=CH$_2$]-TiCl$_2$ (**1**) [7].
(b) Synthesis of Me$_2$Si(OCH$_2$CH$_2$CH$_2$SiMe$_2$CH$_2$CH$_2$SiMe$_2$[η^5-C$_5$H$_4$]Ti[η^5-C$_5$H$_5$]Cl$_2$)$_2$ (**2**).

To 0.7 g (2.39 mmol) (OCH$_3$CH$_2$CH$_2$SiMe$_2$CH$_2$CH$_2$SiMe$_2$H)$_2$ and 2.18 g (4.78 mmol) (η^5-C$_5$H$_5$)[η^5-C$_5$H$_4$SiMe$_2$CH=CH$_2$]TiCl$_2$ 20 ml THF is added. At 50 °C two drops of Karsted catalyst are added and the mixture was stirred at 70 °C for 12 h. Then again some drops of the catalyst were added to the mixture and stirred at 70 °C for 4 h. Then the volatile products were distilled off in HV and 2.29 g (2.39 mmol, 100%) of the red, metallic bright metallocene **2** are separated.

Elemental analysis for C$_{40}$H$_{68}$Cl$_4$O$_2$Si$_5$Ti (958.3) (%): Anal. Calcd.: C, 50.13; H, 7.09. Found: C, 50.15; H, 7.05.

IR (NaCl) (cm^{-1}): ν_{SiC} 1253 (vs); ν_{SiO} 1058 (vs).

^{1}H NMR in CDCl$_3$ (δ): 0.05 (m, 6H, Me$_2$SiCH$_2$CH$_2$SiMe$_2$), 0.4 (s, 6H, Me$_2$SiO), 0.6 (m, 4H, OCH$_2$CH$_2$CH$_2$Si), 1.6 (m, 4H, OCH$_2$CH$_2$CH$_2$Si); 3.6 (m, 4H, OCH$_2$CH$_2$CH$_2$Si); 6.56 (s, 10H, C$_5$H$_5$); 6.63 (pt, 4H, C$_5$H$_4$, $^3J_{HH}$ = 2.3 Hz); 6.90 (pt, 4H, C$_5$H$_4$, $^3J_{HH}$ = 2.3 Hz).

^{13}C{^{1}H} NMR in CDCl$_3$ (δ): 0.1 (Me$_2$Si); 0.5 (Me$_2$Si),1.3 (Me$_2$SiO); 4.1 (Me$_2$SiCH$_2$CH$_2$SiMe$_2$); 7.3 (Me$_2$SiCH$_2$CH$_2$SiMe$_2$); 16.1 (OCH$_2$CH$_2$CH$_2$ SiMe), 28.6 (OCH$_2$CH$_2$CH$_2$SiMe); 65.2 (OCH$_2$CH$_2$CH$_2$SiMe); 122.3 (C$_5$H$_5$), 122.7, 123.9 (C$_5$H$_4$), 131.8 (*ipso*C–C$_5$H$_4$).

(c) Synthesis of **3** (η^5-C$_5$H$_5$)$_2$Ti(Cl) (C≡CSiMe$_3$).

To the solution of 1.9 g (3.0 ml, 18 mmol) HC≡CSiMe$_3$ in 20 ml THF at −70 °C 7.35 ml BuLi (18 mmol, 2.5 M solution in hexane) were added. After 5 min the mixture is warmed up

within 1 h at 25 °C. Then 4.55 g (18 mmol) $(\eta^5\text{-}C_5H_5)_2TiCl_2$ are added and stirred for 10 min. All volatile compound are distilled off in HV. To the residue ether is added and the solution filtered on silicagel. The ether is evaporated and 3.13 g (10.1 mmol, 56%) yellow orange solid titanocene **3** was produced.

Elemental analysis for $C_{15}H_{19}ClSiTi$ (310.70) (%): Anal. Calcd.: C, 58.06; H, 6.18. Found: C, 58.61; H, 6.74.

IR (KBr) (cm^{-1}): $\nu_{C\equiv C}$ 2018 (w).

^{1}H NMR in CDCl$_3$ (δ): 0.14 (s, 9H, C≡CSi$\underline{Me_3}$); 6.43 (s, 10H, C$_5$H$_5$).

^{13}C{^{1}H} NMR in CDCl$_3$ (δ): 1.4 (C≡CSiMe$_3$); 116.8 (C$_5$H$_5$), 133.8 (C≡CSiMe$_3$); 166.4 (C≡CSiMe$_3$).

EI-MS (*m/z* (relative intensity)): 310 (7), M$^+$; 274 (96), M$^+$–Cl; 178 (100), M$^+$–C≡CSiMe$_3$.

(d) Synthesis of **4** $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$ [8].

2.2. Syntheses of heterogeneous Ti and Zr metallocene catalysts for ethylene and propylene polymerisation

Commercially available montmorillonite K10 (Südchemie, Moosburg, Germany) was dried for 2 h under argon or nitrogen at 200 °C, kaolin in vacuum for 4 h. Surface fixed alumoxanes were produced by reactions of TIBA or TMA with the dried carrier in toluene suspension. The reaction times with montmorillonite was 2 h and with kaolin 3 days. The solvent was filtered and the residue washed twice with heptane to extract impurities. Then a solution of the metallocene catalyst in toluene was added. After 1 h reaction time (with montmorillonite) and 4 h (with kaolin) the heterogeneous metallocene catalysts were filtered and again washed twice with toluene.

These catalysts can be used immediately for ethylene or propylene polymerisation. No further additives are necessary for olefin polymerisation. The catalysts can also be stored; after 1 week at 7 °C the activity did not change.

The ethylene polymerisation proceeded in heptane solution in a 1 l Büchi autoclav usually at 10 bar ethylene pressure. The polymerisation time was 1 h.

For propylene polymerisation 250 ml propylene was condensed in the 1 l reactor. For purification of the propylene 12 mmol TIBA was added. The heterogeneous catalyst system was suspended in 10 ml toluene and was transferred under argon pressure (6 bar) into the reactor which was filled with liquid propylene. After reaching the reaction temperature the polymerisation continued for 1 h before it was stopped.

3. Results

Heterogeneous catalysts were produced with kaolin as inorganic carrier from Cp$_2$ZrCl$_2$, Cp$_2$ZrHCl or Cp$_2$TiCl$_2$ and TMA as cocatalyst. These catalysts were active in ethylene polymerisation (Table 1), but not in propylene polymerisation. The three heterogeneous catalysts are not as active as the homogeneous catalysts are, but the molecular weights of the PE formed are higher than those of the homogeneous catalysts.

Table 1
Ethylene polymerisation with homogeneous and heterogeneous Ti and Zr metallocenes on kaolin[a]

Polymerisation	Catalyst	Activity (kg PE/mol Zr (Ti) h)	$\bar{M}_\eta \times 10^{-6}$ (g/mol)	T_M (°C)
Homogeneous	Cp$_2$ZrCl$_2$	17437	0.30	136.5
	Cp$_2$ZrHCl	15683	0.32	136.7
	Cp$_2$TiCl$_2$	9100	0.37	136.8
Heterogeneous	Cp$_2$ZrCl$_2$	5269	0.38	137.7
	Cp$_2$ZrHCl	4310	0.48	138.4
	Cp$_2$TiCl$_2$	1463	0.90	137.0

[a] Homogeneous: 0.003 mmol Zr (Ti); Al/Zr (Ti) = 2000; cocatalyst: 6 mmol MAO. Heterogeneous: 5 g kaolin, 0.024 mmol Zr (Ti); Al/Zr (Ti) = 500; cocatalyst: 12 mmol TMA. Solvent: 200 ml heptane; ethylene pressure: 10 bar; polymerisation temperature: 50 °C; polymerisation time: 1 h.

Table 2

Heterogeneous ethylene polymerisation on montmorillonite with TMA and TIBA as cocatalysts[a]

Cocatalyst Al (mmol)	Molar ratio of Al/Zr	Activity (kg PE/mol Zr h)	$\bar{M}_\eta \times 10^{-6}$ (g/mol)	T_M (°C)
TMA 6	500/1	5575	0.38	136.1
TIBA 6	500/1	6751	0.35	136.3
TMA 6	1000/1	7253	0.38	136.2
TIBA 6	1000/1	8250	0.34	136.2
TMA 12	2000/1	13508	0.34	136.5
TIBA 12	2000/1	14083	0.38	136.1

[a] Conditions: 5 g montmorillonite; catalyst: Cp_2ZrCl_2; cocatalysts: TMA, TIBA; solvent: 200 ml heptane; ethylene pressure: 10 bar; polymerisation temperature: 50 °C; polymerisation time: 1 h.

Table 3

Propylene polymerisation with homogeneous and heterogeneous rac-Et(Ind)$_2$ZrCl$_2$ catalysts[a]

Catalyst system	Catalyst/system/reaction temperature	Molar ratio of Al/Zr	Activity (kg PE/mol Zr h)	$\bar{M}_\eta \times 10^{-6}$ (g/mol)	T_M (°C)	Tacticity (%)
Homogeneous	4.8 mmol MAO/4.8 μmol Zr/40 °C	1000	5700	32000	140.6	88.9
Heterogeneous	12 mmol TMA/15 μmol Zr/40 °C	800	6800	1500	130.1	83.2
	6 mmol TIBA/1.9 μmol Zr/50 °C	3200	60300	11000	122.8	80.8

[a] Homogeneous: catalyst: rac-Et(Ind)$_2$ZrCl$_2$; cocatalyst: MAO. Heterogeneous: 5 g montmorillonite; catalyst: rac-Et(Ind)$_2$ZrCl$_2$; cocatalysts: TMA, TIBA. Solvent: 250 ml propene; polymerisation time: 1 h.

In contrast to the heterogeneous catalysts on kaolin are the heterogeneous catalysts formed on montmorillonite as inorganic carrier very active in ethylene and propylene polymerisation. In many reactions their activities are higher than the activities of comparable homogeneous catalysts [9,10] (Table 2). The cocatalysts TMA and TIBA have some influence on the polymerisation activities, with TIBA as cocatalyst they are higher than with TMA.

The polymerisation of propylene on montmorillonite was tested with TIBA or TMA as cocatalysts and the Brintzinger catalyst. On montmorillonite rac-Et(Ind)$_2$ZrCl$_2$ is a very active heterogeneous catalyst for ethylene or propylene polymerisations. The activities of these heterogeneous catalysts are remarkably higher than those of comparable homogeneous systems (Table 3). The polymerisation activity increase drastically when the reaction temperature changes from 40 to 50 °C.

The tacticities of the polymers formed with heterogeneous catalysts are not so high than those formed by homogeneous catalysts.

Not only commercially available metallocenes were tested but also two silyl substituted titanocenes **1** and

Table 4

Homogeneous and heterogeneous polymerisation of ethylene with the monomeric and dimeric titanocenes **1** and **2** as catalysts[a]

Ti complex	Catalyst system	Activity (kg PE/mol Ti h)	$\bar{M}_\eta \times 10^{-6}$ (g/mol)	T_M (°C)
1	Homogeneous	1367	0.42	138.8
	Heterogeneous	2750	0.50	138.7
2	Homogeneous	3413	0.48	138.7
	Heterogeneous	9563	0.77	137.8

[a] Homogeneous: catalyst **1**: 0.006 mmol; catalyst **2**: 0.003 mmol (two active titanium centres per molecule); cocatalyst: 12 mmol MAO; Al/Ti = 2000. Heterogeneous: 5 g montmorillonite; catalyst **1**: 0.006 mmol; catalyst **2**: 0.003 mmol (two active titanium centres per molecule); cocatalyst: 12 mmol TIBA; Al/Ti = 2000. Solvent: 200 ml heptane; ethylene pressure: 10 bar; polymerisation temperature: 50 °C; polymerisation time: 1 h.
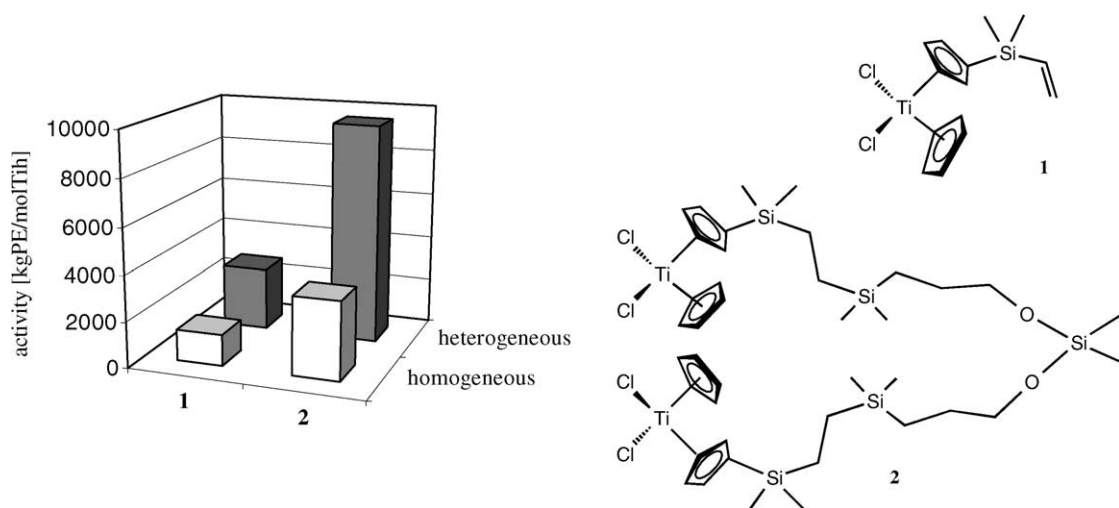
Fig. 2. Activities of homogeneous and heterogeneous ethylene polymerisation of catalysts **1** and **2**.

2 and two alkynyl substituted titanocenes **3** and **4** as catalysts in homogeneous and heterogeneous ethylene polymerisation. The titanocene complexes **1**–**4** were synthesised by Lang et al., University of Chemnitz.

The four titanocene complexes were tested as catalysts in homogeneous and heterogeneous ethylene polymerisations on montmorillonite. The activities of the heterogeneous silyl substituted catalysts **1** and **2** on montmorillonite are higher than those of the homogeneous catalysts (Table 4). Both titanium centres of the heterogeneous bimetallic catalyst **2** are obviously highly activated by the bridge and react with the heterogeneous cocatalyst on the montmorillonite surface [11] (Fig. 2).

The heterogeneous alkynyl substituted titanocenes **3** and **4** are also very active in ethylene polymerisation and form polymers with higher molar masses [8] (Fig. 3, Table 5). Both heterogeneous catalysts are
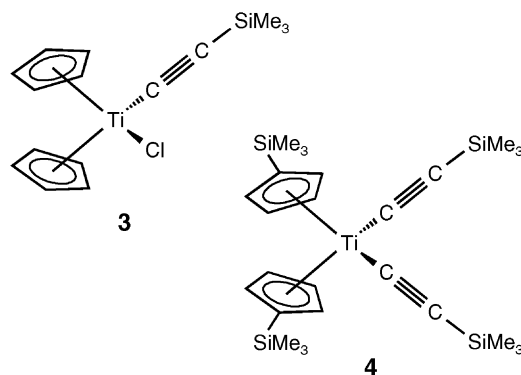

Fig. 3. Alkynyl substituted titanocenes.

Table 5

Homogeneous and heterogeneous polymerisation of ethylene with the alkynyl substituted titanocenes **3** and **4** as catalysts[a]

Ti complex	Catalyst system	Activity (kg PE/mol Ti h)	$\bar{M}_\eta \times 10^{-6}$ (g/mol)	T_M (°C)
3	Homogeneous	2902	0.50	137.5
	Heterogeneous	5715	0.95	135.0
4	Homogeneous	435	0.32	135.4
	Heterogeneous	3580	0.95	135.2

[a] Homogeneous: catalysts **3**, **4**: 0.006 mmol; cocatalyst: 12 mmol MAO; Al/Ti = 2000. Heterogeneous: 5 g montmorillonite; catalysts **3**, **4**: 0.006 mmol; cocatalyst: 12 mmol TIBA; Al/Ti = 2000. Solvent: 200 ml heptane; ethylene pressure: 10 bar; polymerisation temperature: 60 °C; polymerisation time: 1 h.
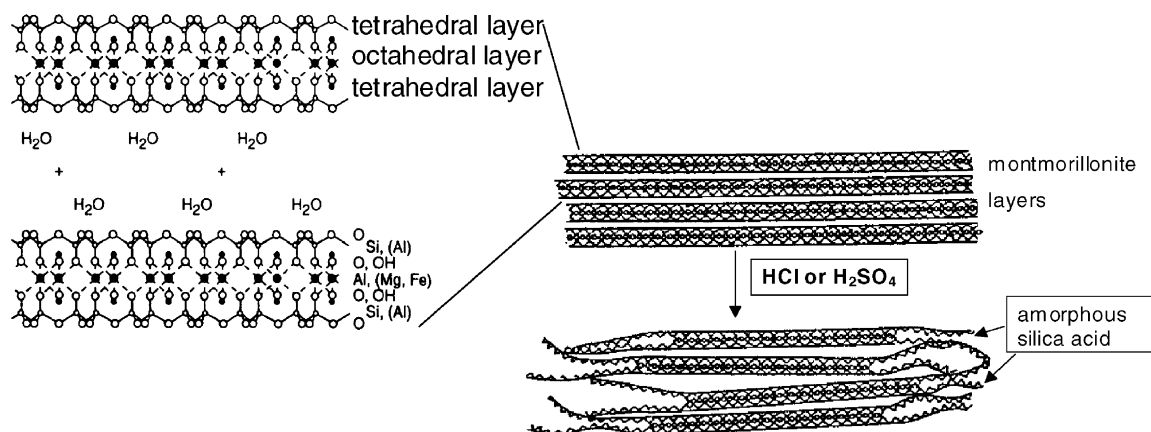
Fig. 4. Disorientation of the montmorillonite layers and formation of silica acid dendrimers by acid treatment.

more active than the homogeneous catalysts and produce PE with significant higher molar masses.

4. Conclusions

The results of the studies on ethylene and propylene polymerisation with heterogeneous titanocene or zirconocene catalysts on kaolin or montmorillonite suggests that montmorillonite forms not the same catalytic centres as kaolin.

The clay mineral montmorillonite has a three-layer structure, with an aluminium octaeder layer which is covered by two silica tetraeder layers; whereas kaolin has only two layers.

For our studies we used the montmorillonite type K10, but we tested also K5, K20 and K30 types of montmorillonite (Südchemie, Moosburg, Germany) with different volumes or distribution of pores as inorganic carrier in ethylene polymerisation.

They produce all similar polyethylenes as the montmorillonite type K10 forms under the same reaction conditions.

Literature studies on clay minerals [12] revealed that montmorillonite is produced from bentonite by HCl or H_2SO_4 treatment at higher temperature. This process solves parts of the aluminium octaeders between the two insoluble silicate layers. By this reaction at the end of the layers moveable silica acids like dendrimers are formed on the montmorillonite surface.

The cocatalysts TIBA or TMA can react with OH groups on these moveable silica acid arms and with the metallocenes to form many surface activated catalysts for ethylene and propylene polymerisation (Fig. 4).

Acknowledgements

References

[1] H. Lang, S. Blau, A. Muth, K. Weiss, U. Neugebauer, J. Organomet. Chem. 490 (1995) C32.
[2] K. Weiss, U. Neugebauer, S. Blau, H. Lang, J. Organomet. Chem. 520 (1996) 171.
[3] K. Weiss, W. Guthmann, S. Maisuls, Heterogene Bimetall-Metathesekatalysatoren aus Carben-komplexen des Fischer Typs und dem reduzierten Phillipskatalysator, Angew. Chem. 100 (1988) 268; Angew. Chem. Int. Ed. Engl. 27 (1988) 267.
[4] K. Weiss, G. Lößel, Darstellung heterogener, metatheseaktiver Carbenkomplexe des Schrock Typs durch Reaktion von Carbinwolfram(VI)komplexen mit Kieselgel, Angew. Chem. 101 (1989) 75; Angew. Chem. Int. Ed. Engl. 28 (1989) 62.
[5] K. Weiss, S. Botzenhardt, M. Hofmann, Ziegler–Natta and metallocene polymerisation of olefins with heterogeneous catalysts, in: W. Kaminsky (Ed.), Metalorganic Catalysts for Synthesis and Polymerisation, Springer, Berlin, 1999, pp. 97–101.
[6] Y. Suga, Y. Maruyama, E. Isobe, T. Suziki, F. Shimizu, EP 0511 665 A2 (1992), to Mitsubishi Kasei Corporation.

[7] D. Seyferth, R. Wyrwa, PCT Int. Appl. WO 97 32,908 [Cl. C08F10/00] (12 September 1997).;
D. Seyferth, R. Wyrwa, PCT Int. Appl. WO 97 32,918 [Cl. C08G77/60] (12 September 1997).

[8] H. Lang, D.S. A George, G. Rheinwald, Coord. Chem. Rev. 101 (2000) 206–207;

H. Lang, D. Seyferth, Z. Naturforschung B 45 (1990) 212.

[9] S. Botzenhardt, Thesis, University of Bayreuth, 1999.

[10] M. Hofmann, Thesis, University of Bayreuth, 2000.

[11] C. Wirth-Pfeifer, Diplomarbeit, University of Bayreuth, 2000.

[12] G. Lagaly, R. Fahn, Ullmanns Encyklopädie der technischen Chemie, Vol. 23, GmbH, Weinheim, 1983, p. 311.