μ-Gels as Support Materials for Dinuclear Olefin Polymerization Catalysts

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ABSTRACT: μ-Gels which consist of poly(organosilicon) networks can be employed as efficient support materials for ethylene polymerization catalyst precursors. Alkylaluminum cocatalysts can be fixed on the μ-gel surfaces using the PHT (''partially hydrolyzed trimethylaluminum'') method. The influence of different aluminum/water ratios on the ethylene polymerization properties of these heterogeneous systems is investigated. Dinuclear silicon bridged zirconium complexes are used as catalyst precursors yielding polyethylenes with broad or bimodal molecular weight distributions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3344–3354, 2008

Key words: metallocene complexes; μ-gels; heterogeneous catalysts; ethylene polymerization; polyethylene

INTRODUCTION

During the past 25 years, metallocene complexes have been extensively studied as catalysts for the homogeneous and heterogeneous polymerization of α-olefins.[1–26] For industrial applications, heterogeneous catalyst systems are preferred since the amount of the expensive cocatalyst MAO[27–35] can be significantly reduced and ''reactor fouling'' is avoided. Catalyst precursors for olefin polymerization have been heterogenized on a huge number of different support materials.[36–59] Silica gels are the most common supports,[36–41] but many other materials like magnesium chloride,[42–45] aluminum oxide,[46–48] charcoal,[49] polypropylene,[50] polystyrene,[51,52] zeolites,[53–57] starch,[58] or even cherry pits[59] were applied. μ-Gels[60–64] are a new type of support material. These poly(organosilicon) networks have been tested by Köppl and coworkers,[65,66] Schmidt et al.,[67] and Helldörfer et al.[68] who anchored mononuclear catalyst precursors on μ-gel surfaces applying the ''PHT method'' (PHT = partially hydrolyzed trimethylaluminum).[67,68] The cocatalyst is thereby directly prepared on the heterogeneous support material. It seemed likely to extend the PHT method employing μ-gels to dinuclear metallocene catalyst precursors, since these catalysts produced polyethylene resins with broad or bimodal molecular weight distributions in the homogeneous ethylene polymerization.[69–72]

EXPERIMENTAL

General considerations

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. Solvents were purified by distillation from appropriate drying reagents. Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). Deuterated solvents (CDCl$_3$, C$_6$D$_6$) for NMR spectroscopy were stored over molecular sieves (3 Å). Cyclopentadiene was freshly distilled from the dimer. The complexes **1** and **2** were prepared according to the procedures described by Ernst and coworkers.[68,69] All other starting materials were commercially available and were used without further purification.

NMR spectra were recorded at 25°C on a Bruker ARX 250 spectrometer. The chemical shifts in the ^{1}H NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CHCl$_3$, δ = 7.15 for C$_6$D$_6$) and in ^{13}C NMR spectra to the solvent signal (δ = 77.0 ppm for CDCl$_3$, δ = 128.0 ppm for C$_6$H$_6$). Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 eV) and a VARIAN MAT 8500 spectrometer. GC/MS spectra were recorded with a HP 5890 gas chromatograph in combination with a HP 5971A mass detector. At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector. GPC measurements were routinely performed with a WATERS 150CV+ instrument at 140°C containing a styragel HT6E column. As a solvent 1,2,4-trichlorobenzene was used. A RI-detector was used for the determina-

tion of the refractive index, and polypropylene samples with known molecular weight distributions served as calibration standards.

General procedure for the synthesis of heterogeneous catalysts of the PHT type

An amount of 1.0 g of finely powdered microgel was suspended in 100 mL of toluene. Trimethylaluminum solution ($2M$ in toluene; 30 mL, 60 mmol) was added via a cannula, and the suspension was heated to 40°C. After 1 h of stirring, the flask with the dispersion was connected to a second one in which the corresponding amount of distilled water was vaporized. Dry argon was passed through both flasks so that the water-steam-saturated argon hydrolyzed the TMA. After cooling to room temperature, a solution of the precatalyst in 20 mL of toluene was added to the viscous mixture. After stirring for 10 min at room temperature, a color change indicated the activation of the catalyst precursor. The heterogeneous catalyst was filtered over a glass frit, washed with n-pentane and dried *in vacuo*. The catalysts were obtained as fine powders (yields: $\sim$ 96%).
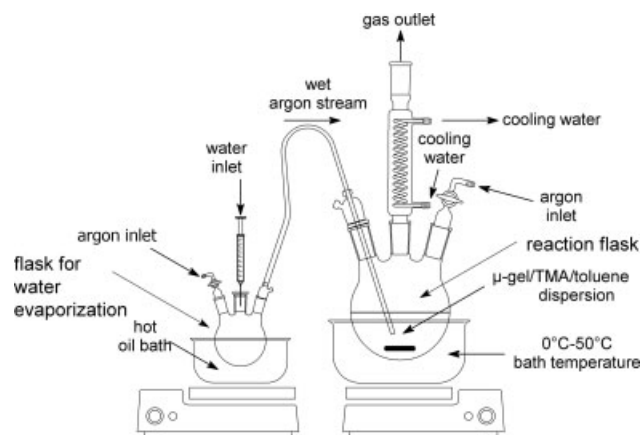
Preparation of silica supported catalysts

An amount of 0.5–10 mg of the catalyst precursor was dissolved (or suspended) in 5–10 mL of toluene and activated with MAO (30% in toluene) so that an aluminum/zirconium ratio of 2500 : 1 was achieved. SiO$_2$ (0.1 g/μmol Zr) was added and the mixture was stirred for 1 h at room temperature. The heterogeneous catalyst was filtered, washed with n-pentane and dried *in vacuo*.

Polymerization of ethylene with heterogeneous catalysts in the 1-L Büchi autoclave

A 1-L Büchi laboratory autoclave was charged with 20 mg to 1.5 g of the desired heterogeneous catalyst. n-Pentane (250 mL) and triisobutylaluminum solution (1 mL, $1M$ in hexanes) were added. The autoclave was thermostated to 60°C, and an ethylene pressure of 10 bar was applied. After 30 min, the pressure was released. The resulting suspension was filtered and the polymer was dried *in vacuo*.

Homogeneous polymerization of ethylene

An amount of 0.5–10 mg of the catalyst precursor was dissolved (or suspended) in 5–10 mL of toluene and activated with MAO (30% in toluene) so that an aluminum/zirconium ratio of 2500 : 1 was achieved. The toluene solution of the catalyst precursor was purged into a Schlenk flask containing 250 mL of n-pentane. The resulting mixture was filled into a

Figure 1 Apparatus for the partial hydrolysis of trimethylaluminum[66] and the preparation of heterogeneous catalysts of the PHT type.

1-L Büchi laboratory autoclave. The autoclave was thermostated at 60°C and purged with ethylene (10 bar). After 1 h, the ethylene feed was stopped, the autoclave was cooled to room temperature and the pressure was released. The resulting polyethylene was filtered and dried *in vacuo*.
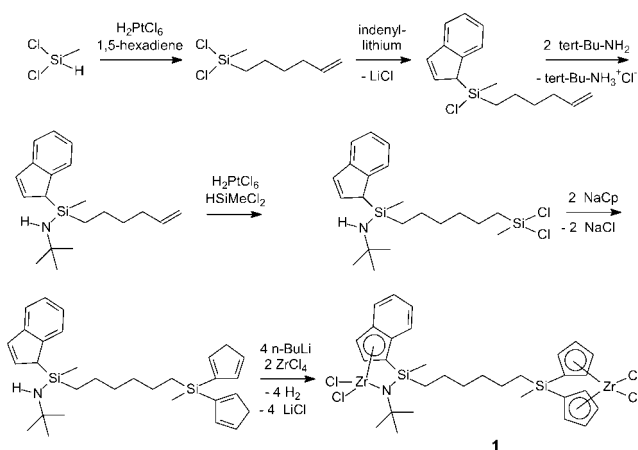
RESULTS AND DISCUSSION

General remarks

μ-Gels can be described as poly(organosilicon) networks consisting of monodisperse spheric particles with sizes between 5 and 100 nm. The molecular weights are in the range of 10^6 to 10^7 kg/mol with small polydispersities between 1.04 and 1.13. Determination of the particle surfaces and volumes gave values around 900 nm^2 and 2500 nm^3, respectively.[60–64] Compared to silica gels, μ-gel particles are smaller by a factor of 1000. Surface measurements applying the BET method yielded values of $\sim$ 350 m^2/g. μ-Gels can be prepared by μ-emulsion polycondensation reactions. Their surfaces can be functionalized, e.g., with alkyl groups or also with metallocene complexes.

Applying the PHT method for the synthesis of heterogenized cocatalysts requires a controlled and continuous hydrolysis of trimethylaluminum. Köppl et al.[66] and Schmidt et al.[67] developed a procedure where the support material (in this case the μ-gel) and trimethylaluminum are mixed in toluene. In a second reaction vessel a defined amount of water is heated to 150°C. The resulting water steam is slowly purged into the μ-gel/TMA solution applying an argon stream (see Fig. 1).

Schmidt[67] found that especially methyl functionalized μ-gels are appropriate support materials for cocatalysts prepared by the PHT method. Because of these results, only methyl functionalized μ-gel was

Scheme 1 Synthesis of the dinuclear complex **1**.[69]

used for the actual work. While Helldörfer et al.[68] and Schmidt et al.[67] investigated the influence of the water/TMA ratio on the ethylene polymerization properties of mononuclear catalyst precursors, the PHT method using μ-gels as support materials was not applied to dinuclear precatalysts up to now.

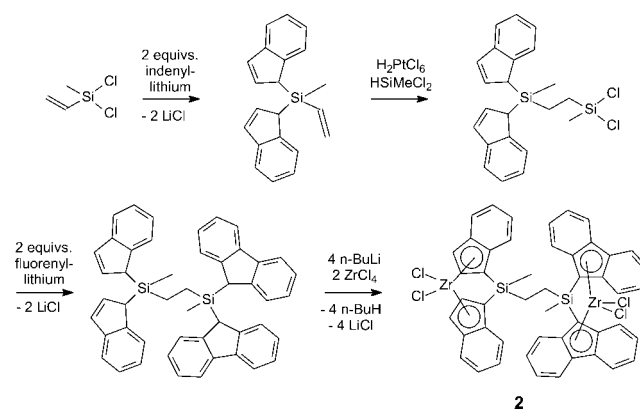## Synthesis of dinuclear zirconium complexes

Two dinuclear complexes were prepared according to the procedure of Ernst and coworkers[69,70] (see Schemes 1 and 2) using hydrosilylation reactions for the coupling of two ligand precursor moieties.

In homogeneous ethylene polymerization reactions, such dinuclear compounds produced polyethylenes with broad or even bimodal molecular weight distributions due to the presence of differently surrounded metal centers in one molecule.[70] Compared with the results of these homogeneous reactions, the polydispersities increase for heterogeneous polymerization reactions when silica is used as a support material.

Synthesis of the heterogeneous cocatalysts and catalysts on microgel basis

According to the PHT procedure of Köppl et al.,[66] heterogeneous cocatalysts were prepared. As support material, methyl functionalized microgel (Wacker Chemie GmbH, Burghausen) was employed. Trimethylaluminum (TMA) initially reacts with Si—OH groups of the support surface under evolution of methane. When the μ-gel surface is covered with partially hydrolyzed TMA species, methane production ceases. By addition of the desired amount of water (Al : H_2O = 0.7–1.4) the formation of cage structures—similar to the structures assumed for MAO—is proposed[27–32,73,74] yielding a heterogenized cocatalyst. Geminal, vicinal, and isolated Si—OH groups may be present on the μ-gel surface

leading to different active sites after reaction with TMA ("site heterogeneity"). According to Sinn and coworkers,[73] the hydrolysis of trimethylaluminum first leads (with evolution of two equivalents of methane) to the unstable dimer $(Me_2Al)_2O$. Immediately, two of these dimeric molecules condense under evolution of one equivalent of trimethylaluminum. Theoretically, four equivalents of methane should be produced from three equivalents of trimethylaluminum, but the ratio TMA : methane found experimentally was 1 : 1.[73] This could only be explained with coordination of "free" TMA to the formed oligomers. As described by Barron and coworkers[28] for the hydrolysis of tri-*tert*-butylaluminum, cage-like molecules of the composition $[Al_6O_6(alkyl)_6]$ containing alternating six-membered $(Al-O)_3$ rings and four-membered $(Al-O)_2$ rings represent energetically optimized structures. Nearly all coordination sites are saturated in these molecules. For "real" MAO, associates like $[Al_6O_6(Me)_6] \cdot 2\ AlMe_3$ or $\{[Al_6O_6(Me)_6]_2 \cdot 4\ AlMe_3\}$ are postulated. Stacking of the basic $[Al_6O_6(Me)_6]$ units leads to "rod-like" macromolecules, while the coordinated trimethylaluminum molecules allow saturation of some remaining free coordination sites.[73] An energetically similar model describes a spherical shell-like structure. In this model a slight coordinative unsaturation is implied leading to a hole in the structure.[73] Sinn[30] and Barron and coworkers[28,29,31,32] suggested that only one of these cage-like structures, namely $[Al_{16}O_{12}(Me)_{24}] = \{[Al_6O_6(Me)_6]_2 \cdot 4\ AlMe_3\}$ containing a trimethylaluminum molecule in its cavity, is able to activate catalyst precursors in an appropriate way. Because of the low content of the necessary MAO species in homogeneous solutions due to dynamic equilibria, a high excess of MAO has to be applied. A great deal of work has been spent on the determination of the active species in metallocene/MAO catalyzed α-olefin polymerizations.[27–35,74–78] The interactions of the MAO cages with TMA were studied computationally by Zurek

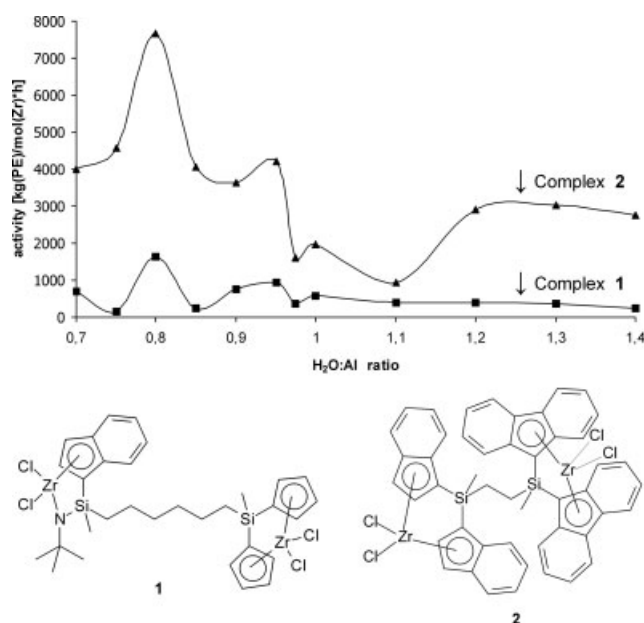**Scheme 2** Synthesis of the dinuclear complex **2**.[70]

and coworkers.[74,75] They found that the coordination of up to two molecules of ''free'' TMA to idealized MAO cages $(AlOMe)_n$ (n = 6–11) is energetically favorable. The ring strain in these molecules is considered to be responsible for the exceptionally high Lewis acidity. Since four-coordinate aluminum centers are not thought to be highly Lewis acidic, Barron et al.[31] developed the concept of latent Lewis acidity (LLA) which can be estimated qualitatively as the sum of the angular distortions found for all atoms of the cage. As a result, the least stable sites of the cage are the most Lewis acidic. Taking into account the known computational and experimental data, the polymerization active species contains a MAO cage to which at least one TMA molecule is coordinated. Depending on the amount of TMA, different species can be proposed for the metallocene moiety. At low TMA concentrations, the cationic metal center may be coordinated to an oxygen atom of the MAO cage representing a ''dormant'' species. Another dormant compound would consist of a dimethylated neutral metal center bound to a MAO cage over a μ-methyl group.[77] Therefore, higher amounts of TMA are necessary to obtain polymerization active catalysts. The most probable polymerization active species consists of an MAO cage and a cationic metallocene moiety which are bridged by a TMA molecule. However, an olefin molecule is necessary for ion-pair separation due to high dissociation barriers obtained for the adduct.[77]

For the synthesis of PHT on μ-gels, similar assumptions can be made. In contrast to the preparation of MAO, the μ-gel support acts as a template (''core-shell model,'' see Refs. 68,79,80) and favors the formation of MAO cages[75] leading to a distinctively higher number of cages compared with homogeneous solutions. As a result, the required amount of trimethylaluminum is reduced dramatically. Choosing the right H_2O : Al ratios for the cocatalyst preparation, the best activities for a given catalyst precursor can be achieved due to the formation of a suitable MAO structure needed for the activation. The optimum ratio is different for each selected catalyst precursor. The complexes **1** and **2** were activated by addition to the PHT/μ-gel/toluene dispersions. After stirring for 30 min, the heterogeneous catalysts were isolated by filtration and dried. For ethylene polymerization experiments, the powder-like catalysts were suspended in *n*-pentane.

Results of ethylene polymerization reactions

Polymerization activities

For comparison with the results of Ernst,[69,70] an optimization of the aluminum/water ratio is necessary. The polymerization runs were routinely performed

Scheme 3 Polymerization activities of complexes **1** and **2** heterogenized on PHT/μ-gel at different H_2O : Al ratios. Polymerization conditions: 250 mL *n*-pentane, 60°C, 30 min, Al : Zr = 250 : 1, 10 bar ethylene, 1 mL TIBA (1*M* in hexanes).

at a temperature of 60°C over 30 min employing an ethylene pressure of 10 bar. Triisobutylaluminum (TIBA) was added as a scavenger. For the preparation of the microgel-supported catalyst, an aluminum/zirconium ratio of 250 : 1 was applied. The water/aluminum ratios were varied between 0.7 and 1.4. Selected polyethylene samples resulting from the most active catalysts were charaterized by HT-GPC.

The ethylene polymerization activities for complexes **1** and **2** as a function of the water/aluminum ratio are given in Scheme 3. The polymerization data are summarized in Tables I and II.

Theoretically, curves with two local maxima would be expected for the ethylene polymerization activities of both complexes, since the differently surrounded metal centers should require different optimum ratios to reach their highest activities. As can be seen from Scheme 3, the theoretical prediction does not fit exactly to the obtained curves since there are more than two local maxima and minima. Interestingly, both activity curves look very similar. The highest activity (1640 kg PE/mol Zr h) of precatalyst **1** was found at a water/aluminum ratio of 0.8, another local activity maximum was observed at a ratio water/aluminum of 0.95 (see Table I). At higher ratios, the polymerization activity decreases continuously. If the water/aluminum ratio goes below 0.7, the cocatalyst is not heterogenized completely. Therefore, polymerization activities obtained with such low ratios are less significant. For comparison purposes, complex **1** was heterogenized on

TABLE I
Ethylene Polymerization Results for the Dinuclear Zirconium Complex 1

H$_2$O : Al	Polymerization activity (kg PE/mol Zr h)	M_n (g/mol)	M_w (g/mol)	PD
0.7	682	–	–	–
0.75	141	–	–	–
0.8	1643	96,760	2,883,400	29.8
0.85	243	–	–	–
0.9	750	–	–	–
0.95	925	89,120	1,178,700	13.2
0.975	363	–	–	–
1.0	584	80,730	5,038,000	62.4
1.1	400	–	–	–
1.2	395	97,720	823,660	8.4
1.3	351	–	–	–
1.4	236	–	–	–
PHT/silica 0.95	597	70,310	1,117,900	15.9
Homogeneous[a]	4652	–	505,500	6.2
Supported on silica only[a]	3650	–	406,950	12.2

Solvent: 250 mL n-pentane, Al : Zr = 250 : 1, 60°C, 30 min, 10 bar ethylene, 1 mL TIBA (1M in hexanes).
[a] Polymerization conditions: activator: MAO (30% in toluene), Al : Zr = 2500 : 1.

PHT/silica (H$_2$O : Al = 0.95) instead of PHT/microgel, while all other reaction parameters remained constant. A maximum activity of 597 kg PE/mol Zr h was obtained. This result indicates that microgels may be useful support materials for these type of catalysts, since the activity increased by a factor of 3 compared with the data obtained for the commonly used silica support. At the same water/aluminum ratio of 0.95, the polymerization activity of the microgel supported catalyst was determined to 925 kg PE/mol Zr h, which is still nearly twice as high as found for the silica supported catalyst. However,

in a homogeneous medium (4650 kg PE/mol Zr h) or heterogenized only on silica (3650 kg PE/mol Zr h), significantly higher activities could be achieved with complex **1**, though higher zirconium/aluminum ratios (1 : 2500) were employed using MAO (30% in toluene).

For precatalyst **2**, a similar polymerization behavior was observed (see Scheme 3 and Table II). A maximum activity of 7650 kg PE/mol Zr h was reached at a water/aluminum ratio of again 0.8. At ratios of 0.95, 1.0, and 1.3, three local activity maxima were found. Applying ratios higher than 1.3, the

TABLE II
Ethylene Polymerization Results for the Dinuclear Zirconium Complex 2

H$_2$O : Al	Polymerization activity (kg PE/mol Zr h)	M_n (g/mol)	M_w (g/mol)	PD
0.7	4000	–	–	–
0.75	4586	–	–	–
0.8	7652	156,090	5,615,500	36.0
0.85	4070	–	–	–
0.9	3628	–	–	–
0.95	4203	115,400	3,018,000	26.2
0.975	1614	–	–	–
1.0	1964	108,620	8,538,000	78.6
1.1	929	–	–	–
1.2	2895	221,740	13,555,000	61.1
1.3	3019	–	–	–
1.4	2753	–	–	–
PHT/silica 0.95	2794	–	5,076,600	26.4
Homogeneous[a]	6840	–	780,300	3.8
Supported on silica only[a]	9940	–	790,700	5.3

Solvent: 250 mL n-pentane, Al : Zr=250 : 1, 60°C, 30 min, 10 bar ethylene, 1 mL TIBA (1M in hexanes).
[a] Polymerization conditions: activator: MAO (30% in toluene), Al : Zr = 2500 : 1.

polymerization activity decreases continuously. When complex **2** was heterogenzied on PHT/silica ($H_2O : Al = 0.95$; in analogy to complex **1**), an activity of 2795 kg PE/mol Zr h was determined. Therefore, complex **2** on microgel support gave significantly higher polymerization activities for most of the applied water/aluminum ratios (see Scheme 3 and Table II). Interestingly, the maximum activity of 7650 kg PE/mol Zr h (at a ratio $H_2O : Al = 0.95$) exceeds the activity of the homogeneous catalyst (6840 kg PE/mol Zr h). However, the highest activity for complex **2** was obtained when only silica was used as support material (9940 kg PE/mol Zr h). For both the homogeneous and the silica supported catalysts, again MAO (30% in toluene) was applied for activation ($Al : Zr = 2500 : 1$). These activity values should always be discussed taking into account the high excess of MAO needed for appropriate activation of the catalyst precursor.

Both catalysts **1** and **2** show their maximum activity at a ratio $H_2O : Al = 0.80$. It can be assumed that at this point the cocatalyst is completely heterogenized while at lower ratios the number of cages also decreases. Due to the dinuclear nature of the precursors, another local activity maximum was expected for both precursors at somewhat different $H_2O : Al$ ratios. The second maxima were found for both catalysts at $H_2O : Al = 0.95$. While the activity of complex **1** decreased at higher $H_2O : Al$ ratios, two other local activity maxima were found for complex **2** at ratios $H_2O : Al > 1$. This surprising result may be explained with the "core-shell model" presented by Helldörfer et al.[68] After all of the accessible Al-Me groups on the μ-gel support were formally hydrolyzed to give polymerization inactive "aluminum oxide," a second activating layer can grow on this aluminum oxide surface. The polymerization activity increases again due to the formation of new cages from TMA and water which are still present in the solution. Again, the differently surrounded metal centers are assumed to show their optimum activity at differing $H_2O : Al$ ratios and Scheme 3 gives proof for this theory.

Complexes **1** and **2** supported on PHT/μ-gel show remarkable differences in their polymerization behavior compared with the results obtained for the homogeneous catalysts and the silica supported catalysts. While the μ-gel support consists of well defined particles, the structures and particle sizes of commercial silica are nonuniform. However, different kinds of MAO cages can grow on the well-defined μ-gel surfaces ("site heterogeneity").[81] Supporting on silica or on μ-gel ($Al : H_2O = 0.8$) had a beneficial effect on the polymerization activities of complex **2** compared with homogeneous polymerization. Because of the short ethylene spacer group between the silicon bridging atoms, the steric bulk
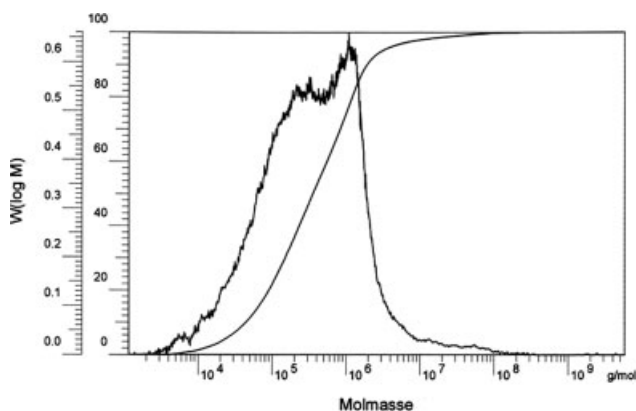
around the zirconium centers increases dramatically when MAO is added. By fixing on a support, the steric bulk seems to be reduced since the Lewis acidic aluminum containing MAO cages also interact with Lewis basic SiOR groups on the support surface. The size of the cavities proposed in the MAO cages[73] may be responsible for the different activities of complexes **1** and **2** after heterogenization. Because of the lower steric bulk around the catalytically active centers and the longer spacer group between them, both the amido part and the bis(cyclopentadienyl) part of complex **1** may be fixed in different alumoxane cavities. According to the particle growth model,[82] the polymer forms a layer around the solid core of the catalyst particle. Diffusion of the monomer into the pores of the support material is then limited resulting in a decreased polymerization rate until the fragmentation of the particle starts. The fragmentation process provides an easier access of the monomer to the active centers and, therefore, to an enhanced activity. Since the fragmentation proceeds from the edge of the macropacrticle to the solid core, this process seems to be quite slow for the heterogenized complex **1**. Another explanation of the reduced activity of complex **1** could be the higher electrophilicity of the amido part preferring a coordination of the metal center to oxygen atoms of the supported cocatalyst ("dormant" species). In contrast, complex **2** with its short spacer group is probably too big for the alumoxane cages of the catalyst surface. A weaker coordination of the catalyst molecules on the heterogeneous cocatalyst is therefore postulated. With regard to the particle growth model, again a polymer layer is growing on the catalyst particle, but the fragmentation process would set free catalytically active centers faster resulting in higher polymerization activity.

Polymer properties

Similar tendencies were observed for the molecular weights M_w obtained for the polyethylenes produced with catalysts **1** and **2**. The molecular weights M_w dropped when increasing the water/aluminum ratio from 0.8 to 0.95 but increased for ratios > 1.0. At these higher ratios, some of the catalytic centers may be destroyed, while the residual active centers produce higher molecular weight polyethylene.

For complex **1**, the highest values for both M_w and PD were obtained at a ratio of 1.0 (see Table I). For this polymer sample, a bimodal molecular weight distribution was obtained (Fig. 2).

The upper molecular weight fraction can be assigned to the half sandwich amido part of the dinuclear catalyst precursor, the lower weight fraction to the silicon bridged bis(cyclopentadienyl) part.

Figure 2 GPC curve of the polyethylene produced with 1/PHT/μ-gel at a H_2O : Al ratio of 1.0 exhibiting bimodal character.

For water/aluminum ratios higher than 1.0, both the molecular weights M_w and the polydispersities PD decrease. Since the amido functionalized metal centers of the dinuclear catalyst are nearly inactive under these polymerization conditions, the resulting polyethylene with lower molecular weight and polydispersity is similar to that one obtained with a single metallocene catalyst.

The highest molecular weight M_w obtained for polyethylenes produced with complex **2** reaches a tremendous value of more than $13.5 \cdot 10^6$ g/mol (at a ratio H_2O : Al = 1.20). Bis(fluorenyl)zirconium catalysts are known to produce high molecular weight polyethylenes but the molecular weight differences compared with analogously substituted bis(indenyl) systems are less obvious in the GPC curves. The higher molecular weight fractions of the polyethylenes produced with **2** can be still assigned to the bis(fluorenyl) moieties but the molecular weight distributions show broad but unimodal curves. In some cases, a shoulder resulting from the lower weight fraction can be detected as shown for the polyethylene produced with **2** at a water/aluminum ratio of 1.0 (see Fig. 3).
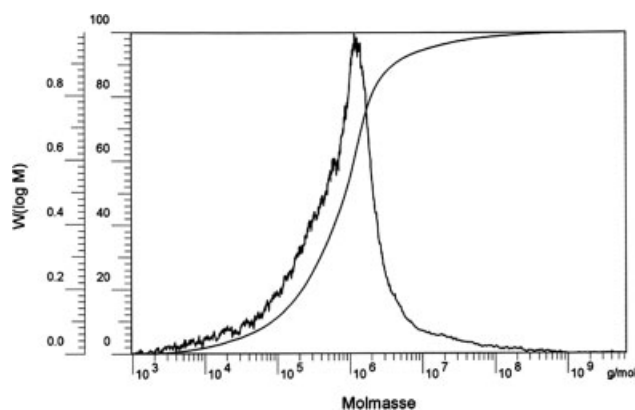
Comparison of the catalytic properties of complexes 1 and 2 with literature known compounds

Since only two dinuclear catalyst precursors were studied, structure–activity relationships[15,83] for μ-gel/PHT heterogenized metallocene complexes are hard to predict. Therefore, some other catalyst precursors prepared in the Alt group are presented for comparison purposes. Different types of mononuclear catalyst precursors supported on microgels have been tested for ethylene polymerization in the Alt group.[65–68] Besides metallocene complexes, also bis(imino)pyridine iron complexes and α,α'-diimine

nickel complexes were employed as precursors. For comparison purposes, the ethylene polymerization results of some selected catalysts are listed in Table III together with the best results obtained for complexes **1** and **2**.
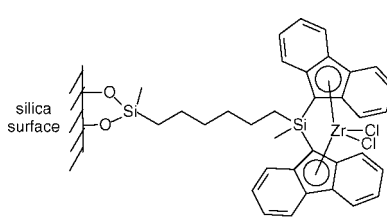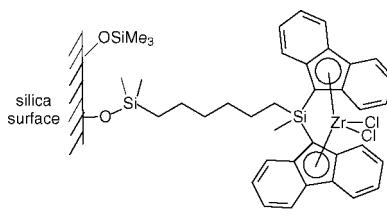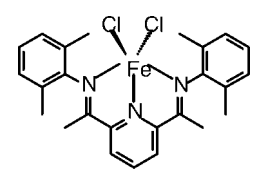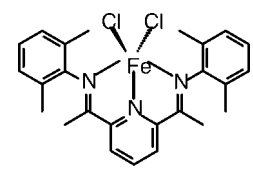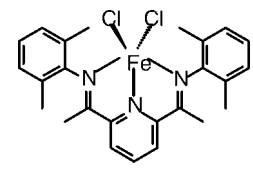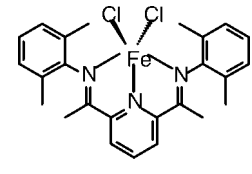
Catalysts **3** and **4** (entries 5 and 6 in Table III) were prepared by Schertl and coworkers[65] who reacted silicon bridged bis(fluorenyl) compounds containing at least one silicon-chloro bond with microgel surfaces. Protection of unreacted Si—OH groups with trimethylchlorosilane and complexation of the bis(fluorenyl) moieties with zirconium tetrachloride gave the microgel supported zirconocene complexes. These complexes contain ''one half'' of complex **2**. Their significantly lower ethylene polymerization activities compared with complex **2** may have two reasons. Both catalysts **3** and **4** exhibit only one metal center per catalyst molecule, the bis(indenyl) part is absent. Another explanation arises from the different treatment of the surface of the support material. While the PHT process leads to aluminum covered microgel particles (=supported cocatalysts), complexes **3** and **4** are fixed directly on the support surface The zirconium centers can therefore coordinate easier to oxygen atoms of the support material after activation with MAO leading to deactivation. The obtained polyethylenes show distinctively lower molecular weights M_w compared with complexes **1** and **2**.

The polymerization behavior of the ''standard'' metallocene complexes zirconocene dichloride (entry 7 in Table III) and bis(n-butylcyclopentadienyl)zirconium dichloride (entries 8–11 in Table III) supported on microgels using the PHT method was investigated by Helldörfer et al.[68] In analogy to complexes **1** and **2**, their polymerization activities show several maxima and minima at different H_2O : Al ratios. Similarly to homogeneous systems, these cyclopenta-

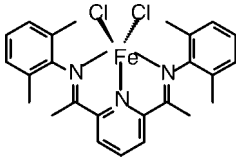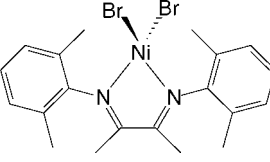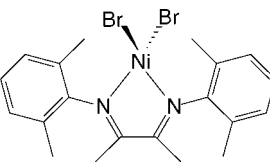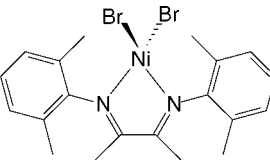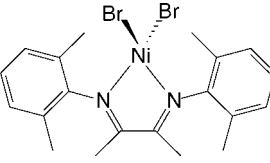**Figure 3** GPC curve of the polyethylene produced with 2/PHT/μ-gel at a H_2O : Al ratio of 1.0 exhibiting a broad monomodal molecular weight distribution with a shoulder.

TABLE III
Comparison of Ethylene Polymerization Results Obtained with Complexes 1 and 2 and Selected Literature Known Mononuclear Complexes

Complex	Support material	H_2O : Al	Polymerization activity (kgPE/mol M h)	M_n (g/mol)	M_w (g/mol)	PD
1	μ-gel	0.8	1643	96,760	2,883,400	29.8
1	μ-gel	1.0	584	80,730	5,038,000	62.4
2	μ-gel	0.8	7652	156,090	5,615,500	36.0
2	μ-gel	1.0	1964	108,620	8,538,000	78.6
3 (structure)	μ-gel	0.85 (MAO, 30% in toluene)	1440	–	640,000	–
4 (structure)	μ-gel	0.85 (MAO, 30% in toluene)	140	–	1,230,000	–
Cp_2ZrCl_2	μ-gel	1.25	6950	211,540	535,200	2.53
$(n\text{-}Bu\text{-}Cp)_2ZrCl_2$	μ-gel	0.90	14,830	185,830	446,000	2.40
$(n\text{-}Bu\text{-}Cp)_2ZrCl_2$	μ-gel	1.0	587	128,780	631,000	4.90
$(n\text{-}Bu\text{-}Cp)_2ZrCl_2$	silica	0.85	2090	119,520	502,000	4.20
$(n\text{-}Bu\text{-}Cp)_2ZrCl_2$	silica	1.0	345	135,430	623,000	4.60
(Fe structure)	μ-gel	0.9	30,020	67,800	800,000	11.8
(Fe structure)	μ-gel	1.0	11,720	52,350	869,000	16.6
(Fe structure)	μ-gel	1.1	21,875	63,750	612,000	9.6
(Fe structure)	silica	1.0	12,500	21,740	400,000	18.4

TABLE III
Continued

Complex	Support material	H₂O : Al	Polymerization activity (kgPE/mol M h)	M_n (g/mol)	M_w (g/mol)	PD
(Fe bis(arylimino)pyridine dichloride complex)	silica	1.1	41,850	87,500	350,000	4.00
(Ni α,α′-diimine dibromide complex)	μ-gel	1.0	2290	75,610	272,200	3.60
(Ni α,α′-diimine dibromide complex)	μ-gel	1.2	2760	112,700	417,000	3.70
(Ni α,α′-diimine dibromide complex)	silica	0.8	2940	91,630	394,000	4.30
(Ni α,α′-diimine dibromide complex)	silica	1.0	2450	78,680	299,000	3.80

Solvent: 250 mL *n*-pentane, Al : Zr =250 : 1, 60°C, 30 min, 10 bar ethylene, 1 mL TIBA (1*M* in hexanes).[65,67,68]

dienyl containing metallocene catalysts produce polyethylenes with lower molecular weights compared with fluorenyl substituted compounds. Because of the mononuclear character of the catalyst precursors, the polydispersities of the polyethylenes are quite low (2.4 < PD < 4.9) compared with PD values of 30–78 for complexes **1** and **2**. If silica is used as the support material instead of microgels, the activities decrease by a factor of 6 indicating the positive effect of the defined spherical structure of the microgel particles.

The bis(arylimino)pyridine iron complex **6** (entries 12–16 in Table III) prepared by Gibson and coworkers[84,85] showed very high polymerization activities (up to 30,000 kg PE/mol M h) when supported on microgels.[68] In contrast to the polymerization behavior of the mononuclear zirconocene complexes, broad molecular weight distributions were obtained for the polyethylenes produced with iron complex **6** both in homogeneous and heterogeneous systems. In analogy to the bis(arylimino)pyridine iron complex **6**, the α,α′-diimine nickel complex **7**[86,87] was supported on μ-gels by Helldörfer et al.[68] Contrarily to the complexes **1** and **2**, the nickel complex showed similar polymerization activities at H₂O : Al ratios ranging from 0.8 to 1.3 (entries 17–20 in Table III). The molecular weight and polydispersity values are also barely affected by changing the H₂O : Al ratio. For this nickel catalyst, the concept of heterogenization on a heterogeneous cocatalyst was not applicable due to weaker interactions of the catalytically active species with the cocatalyst surface resulting in an apparently homogeneous polymerization behavior (reactor "fouling").

CONCLUSIONS

Two dinuclear zirconium complexes were heterogenized on methyl functionalized microgel applying the PHT method. The water/aluminum ratio used for the preparation of the PHT support material had a great influence on both the ethylene polymerization activities and the properties of the resulting polyethylenes. For both catalysts, maximum activities could be determined. In both cases, the polymerization activities for the homogeneous catalysts are distinctly higher compared with the microgel-supported systems. The advantages of the heterogeneous catalysts are extremely high molecular weights, M_w, and higher dispersities of the resulting polyethylenes compared with the homogeneously obtained products. Comparison of the polymerization results with polymer properties obtained for other microgel supported mononuclear catalyst precursors reveal that the dinuclear catalysts exhibit similar polymerization activities, but produced polyethylenes with dramatically increased molecular weights, M_w.

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