

Microgels as New Support Materials for Heterogeneous Cocatalysts in Ethylene Polymerization Reactions

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ABSTRACT: Microgels are monodisperse poly(organosiloxane) microparticles that can be functionalized at their surface. These materials were tested as supports for heterogeneous cocatalysts of the methylaluminoxane type and were used for the polymerizations of olefins with transition-metal catalysts. The cocatalysts were synthesized directly on the surfaces of the microgel particles by the partial hydrolysis of trimethylaluminum and were then used for the activation of homogeneous catalyst precursors. Complexes of various chemical natures were successfully activated and

optimized through variations in the Al/H₂O ratio used for the synthesis. Metallocene dichloride complexes and coordination compounds of iron and nickel were tested as catalysts for ethylene polymerization, and the results were compared with the results for the homogeneous systems and heterogeneous systems supported on silica gel (SiO₂). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3021–3029, 2002

Key words: catalysis; catalysts; polyethylene (PE)

INTRODUCTION

Transition-metal complexes are attractive catalysts for the polymerization of olefins.^{1–6} In combination with a cocatalyst, usually methylaluminoxane (MAO), they reach high productivities under homogeneous conditions. Unfortunately, this homogeneous character of the catalyst systems can cause problems for their technical applications. In many cases, homogeneous catalysts show so-called reactor fouling: the sticking of the formed polymer on the reactor walls. Reactor fouling makes it impossible to run the catalytic polymerization in a continuous process. Therefore, strategies have been developed to heterogenize the catalyst systems to avoid fouling. One possibility is to fix the catalyst on a support material.^{2,7–10} Another way is to heterogenize the cocatalysts.^{11–13} Appropriate supports are various inorganic and organic materials, such as functionalized polystyrene and silica.^{14–17} Recently, new support materials, so-called microgels, were developed.^{18–21} These silicon microgels are an alternative to silica as heterogenization agents for some catalytic processes.^{22–25} In particular, a microgel functionalized with methyl groups on its surface proved to be very efficient.^{23,24}

On the basis of these earlier investigations, we developed a universal heterogeneous cocatalyst of the MAO type by synthesizing the cocatalyst directly on the surface of a methyl microgel. This heterogeneous cocatalyst was able to activate transition-metal catalyst precursors of different chemical natures and could be optimized for each catalyst system by the synthesis conditions being varied.

RESULTS AND DISCUSSION

Synthesis of the heterogeneous cocatalysts

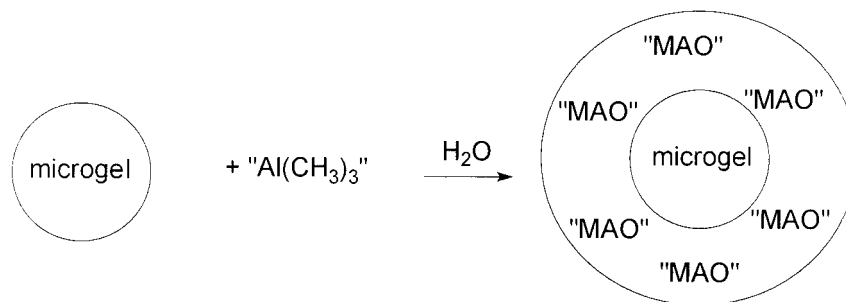
For the synthesis of heterogeneous cocatalysts based on partially hydrolyzed trimethylaluminum (TMA), it was necessary to ensure that the water and TMA were reacting slowly in a nearly homogeneous manner. Therefore, TMA was hydrolyzed, with a water-saturated argon stream passing through a dispersion of the methyl-functionalized microgel and TMA in toluene. This procedure allowed the synthesis of the cocatalyst directly on the surface of the support materials and variations of the compositions of the cocatalysts with different amounts of water, TMA, and support (Scheme 1).

In the same way, it was also possible to synthesize heterogeneous cocatalysts supported on silica with a TMA/silica/toluene suspension.^{22,26}

Both heterogeneous cocatalyst systems, supported on microgel or silica, were used for the activation of various transition-metal complexes and were tested for the polymerization of ethylene.

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Scheme 1 Synthesis of a heterogeneous cocatalyst supported on a microgel particle.

Synthesis of the heterogeneous catalyst systems

The cocatalyst suspensions could be used directly for the activation of transition-metal complexes to give heterogeneous catalyst systems for the polymerization of ethylene. For this purpose, a certain amount of the complex was added to the cocatalyst suspension. In all cases, the ratio of the transition metal to aluminum was 1/250. The activated catalysts heterogenized by ionic interactions of the catalyst cation and the negatively charged cocatalyst (Scheme 2).

The heterogeneous catalysts were then isolated by filtration and dried in vacuo.

To develop a universal heterogeneous cocatalyst, we activated catalyst precursors of different chemical natures: an unbridged zirconocene dichloride complex (**A**);²⁷ a coordination compound of iron (**B**), as established by Gibson et al.²⁸ for the polymerization of olefins; and a nickel complex (**C**) of the so-called Brookhart type^{29,30} (Fig. 1).

All these catalyst precursors were activated successfully and were used for the polymerization of ethylene.

Polymerization of ethylene with the heterogeneous catalyst systems

To optimize the heterogeneous catalyst systems, we investigated the dependence of the catalytic activities on the amount of water used for the cocatalyst synthesis. The other parameters, including the transition-

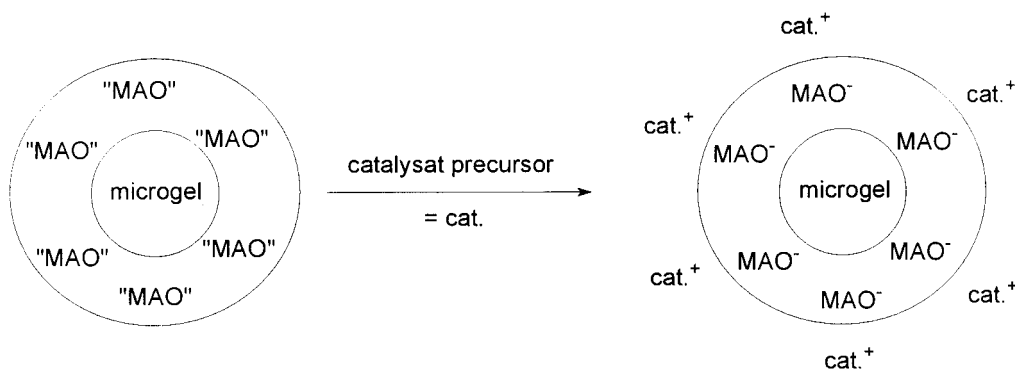
metal/aluminum ratio, the ethylene pressure, the solvent, the polymerization duration, and the polymerization temperature, remained constant for all experiments. The results obtained with the catalyst systems supported on microgels were compared with the results for systems that were heterogenized in an analogous manner on silica (SiO_2) and with the results for the polymerizations in homogeneous solutions. All the results are listed in Table I.

A closer look at the activities in correlation to the water/aluminum ratio used for the synthesis of the heterogeneous cocatalysts reveals clear effects. For the catalyst precursor **A**, a maximum for the activity was observed with an $\text{H}_2\text{O}/\text{Al}$ ratio of 0.90 (Fig. 2).

The activity of the microgel-supported catalysts was seven times higher than the activity of the corresponding silica (SiO_2) systems. Nevertheless, the activity observed for the homogeneous case with 38,220 g of polyethylene (PE)/mmol of catalyst \times h was more than twice as high. This high activity of the homogeneous polymerization, however, required a 10 times higher Al/Zr ratio of 2500/1 instead of the 250/1 ratio for the heterogeneous systems.

The activity of microgel-supported **B** showed two local maxima depending on the $\text{H}_2\text{O}/\text{Al}$ ratio, the first one at an $\text{H}_2\text{O}/\text{Al}$ ratio of 0.90 and the second at a ratio of 1.10 (Fig. 3).

The first maximum at 0.90 (30,020 g of PE/mmol of catalyst \times h) was a little bit higher than the second one



Scheme 2 Heterogenization of a transition-metal catalyst

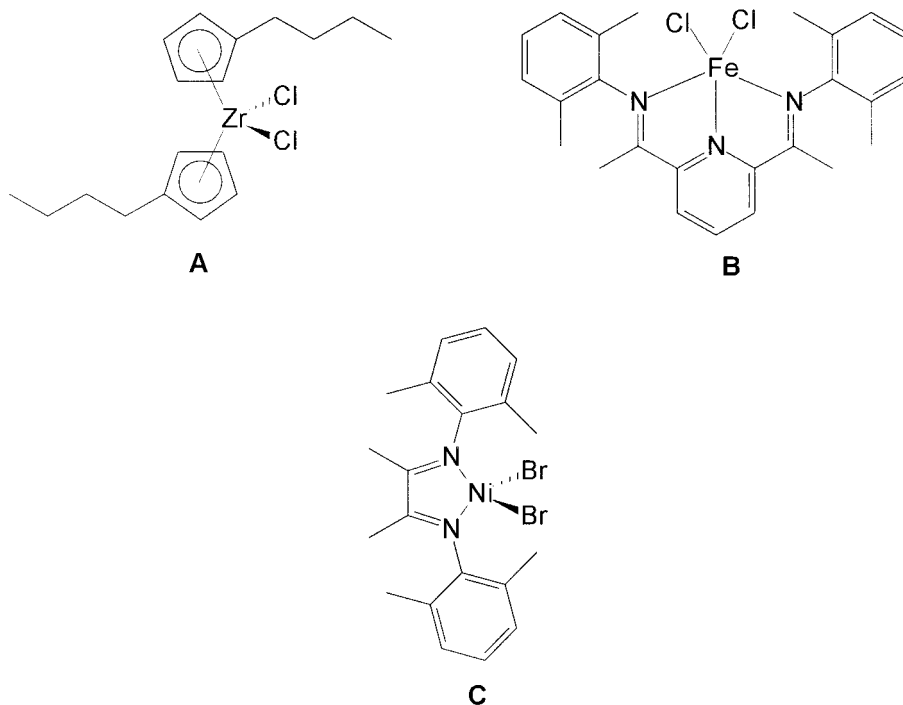


Figure 1 Catalyst precursors tested for the activation and heterogeneous polymerization of ethylene.

at 1.10 (21,875 g of PE/mmol of catalyst \times h). The polymerization experiments performed with catalysts supported on silica showed only one maximum for the activity at an $\text{H}_2\text{O}/\text{Al}$ ratio of 1.10 with 41,850 g of PE/mmol of catalyst \times h. In the homogeneous polymerization, the catalyst precursor **B** reached an activity of 50,220 g of PE/mmol of catalyst \times h ($\text{Al}/\text{Fe} = 2500/1$).

The catalyst precursor **C** did not show clear dependencies of the activities when supported on heterogeneous cocatalysts that were prepared with different $\text{H}_2\text{O}/\text{Al}$ ratios (Fig. 4).

Both heterogeneous systems, microgel and silica-supported, provided almost the same activities within the experimental error. In addition, the heterogeneous catalysts were more than two times more active than the homogeneous catalysts. During all polymerizations with **C**, strong reactor fouling was observed.

An explanation for these observed effects can be found in the activating impact of the cocatalyst MAO. MAO is not a defined compound. In a homogeneous solution of MAO, various species can be observed. The scale of MAO species ranges from low molecular oligomers in the form of chains or cycles up to cages of different sizes. Also, free TMA appears in low concentrations.^{31–38} All MAO species can be transformed into one another in dynamic equilibrium reactions mediated by TMA. Sinn³⁹ and Barron et al.^{40–43} suggested that only one MAO species is able to activate a transition-metal catalyst precursor in an appropriate way. This species should be an $[\text{Al}_{16}\text{O}_{12}\text{Me}_{24}]$ cage with a

TMA molecule in its cavity. After activation of a catalyst precursor, the active species is stabilized by this cage (Fig. 5).

Ziegler and coworkers^{44,45} refined the theory with various calculations for the stability of such MAO cages.

Because of the low concentration of the right MAO species that alone is able to activate a catalyst precursor, a high molar excess of the cocatalyst is needed in a homogeneous polymerization.

If the cocatalyst is synthesized directly on the surface of a support material, the support acts as a template and favors the formation of MAO cages.⁴⁴ If we choose the right $\text{H}_2\text{O}/\text{Al}$ ratio for the cocatalyst preparation, the best activities can be achieved by the formation of the MAO structure needed for the activation of the catalyst precursor. Therefore, in the case of **A**, a maximum activity was found for an $\text{H}_2\text{O}/\text{Al}$ ratio of 0.90. At this point, the cocatalyst composition led to an optimal activation of the catalyst precursor. At the same $\text{H}_2\text{O}/\text{Al}$ ratio of 0.90, **B** also showed a local maximum for the activity. It can be suggested that in the range of an O/Al composition of 0.90 in the cocatalyst, the activation of a transition-metal catalyst proceeds completely. In addition to the first maximum, **B** showed a second one at an $\text{H}_2\text{O}/\text{Al}$ ratio of 1.10. At this point, the structure of the cocatalyst was again ideal for the activation reaction. This effect could be the result of the formation of a second activating layer on the surface of the cocatalyst particle (Scheme 3).

TABLE I
Results of the Heterogeneous and Homogeneous Polymerization Experiments^a

Catalyst precursor	Support material	H ₂ O/Al	Activity (g of PE/mmol of catalyst × h)	M _w (kg/mol)	D ^b
A	Microgel	0.60	1,820	534	3.3
A	Microgel	0.70	2,275	515	3.9
A	Microgel	0.80	865	745	5.7
A	Microgel	0.85	3,730	624	3.7
A	Microgel	0.90	14,830	446	2.4
A	Microgel	0.95	2,457	723	5.2
A	Microgel	1.00	587	631	4.9
A	Silica	0.70	450	523	3.5
A	Silica	0.80	1,200	678	7.3
A	Silica	0.85	2,090	502	4.2
A	Silica	0.90	1,070	590	3.7
A	Silica	0.95	670	710	5.3
A	Silica	1.00	345	623	4.6
B	Microgel	0.85	2,180	119	3.9
B	Microgel	0.90	30,020	800	11.8
B	Microgel	0.95	12,390	631	14.1
B	Microgel	1.00	11,720	869	16.6
B	Microgel	1.05	13,280	581	13.8
B	Microgel	1.10	21,875	612	9.6
B	Microgel	1.15	3,790	136	4.6
B	Microgel	1.20	3,790	148	3.8
B	Microgel	1.30	5,580	395	8.7
B	Silica	0.75	4,230	355	15.0
B	Silica	1.00	12,500	400	18.4
B	Silica	1.05	25,870	335	4.2
B	Silica	1.10	41,850	350	4.0
B	Silica	1.15	23,400	326	10.1
B	Silica	1.20	11,750	405	8.9
C	Microgel	0.80	2,640	263	4.3
C	Microgel	0.85	2,080	185	2.6
C	Microgel	0.90	2,110	256	3.6
C	Microgel	1.00	2,290	272	3.6
C	Microgel	1.10	2,640	344	5.1
C	Microgel	1.20	2,760	417	3.7
C	Microgel	1.30	2,700	339	3.4
C	Silica	0.80	2,940	394	4.3
C	Silica	0.85	2,510	298	3.7
C	Silica	0.90	2,450	328	3.7
C	Silica	1.00	2,450	299	3.8
C	Silica	1.10	1,890	388	4.3
C	Silica	1.20	1,810	113	3.6
A	—	—	38,220 ^c	48.6	5.8
B	—	—	50,220 ^c	95.0	13.2
C	—	—	1,230 ^c	10.9	2.5

M_w = weight average molecular weight; M_n = number-average molecular weight.

^a Polymerization conditions: 60°C, 250 mL pentane, Al/transition metal = 250/1, 10 bar of ethylene, 1 ml of triisobutyl-aluminum, 1 h.

^b D = polydispersity (M_w/M_n).

^c Activation with MAO in the homogeneous phase (Al/transition-metal = 2500/1).

This second maximum could not be found for the zirconocene derivative **A** because of the strong oxophilic nature of zirconium. More water used for the cocatalyst preparation also meant more oxygen in the catalyst system. This caused more deactivating reactions at the zirconium center.

The concept of the heterogenization of a catalyst by a heterogeneous cocatalyst only works if the ionic interactions between the catalyst and cocatalyst are

big enough to hold the catalytic active species on the surface of the cocatalyst. In the case of **C**, for which strong fouling but high activities were found for the heterogeneous systems, the catalyst seemed to work almost independently of the cocatalyst. The result was apparently a homogeneous behavior of the catalyst, and the polymer was not formed on the cocatalyst surface but in a homogeneous solution, leading to reactor fouling. The high activities of the heteroge-

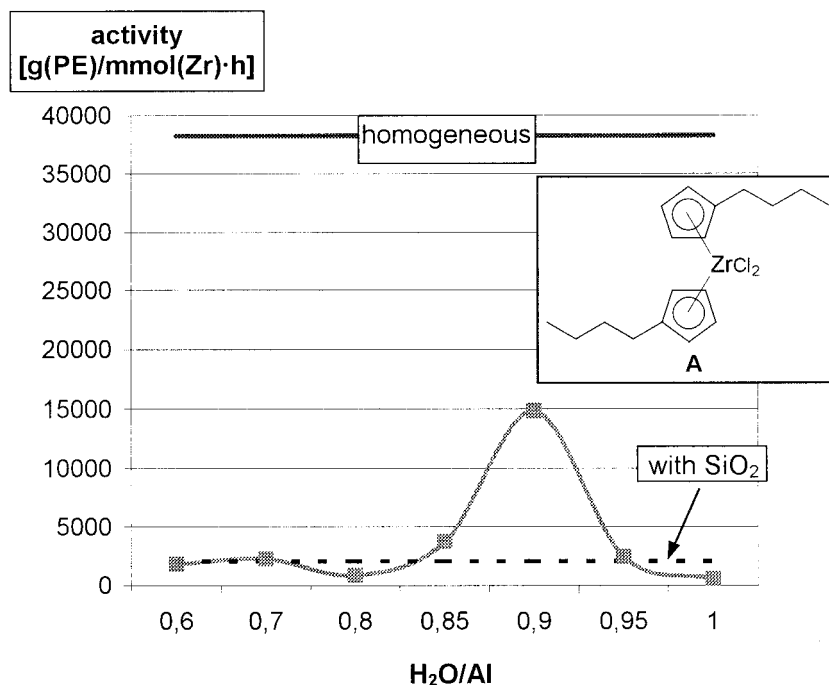


Figure 2 Dependence between the activity and $\text{H}_2\text{O}/\text{Al}$ ratio for **A** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of 60°C , 250 mL of pentane, 1 mL of triisobutylaluminum, $\text{Zr}/\text{Al} = 1/250$, and a time period of 1 h. The maximum activities obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

neous systems can be related to another activating MAO species that has no cage structure and should not strongly interact with the active species. The comparatively low activity for the homogeneous polymerization with **C** suggests that the activating MAO species does not have a complex structure. Too bulky

MAO species seem even to deactivate the catalyst. Therefore, the heterogenization enables the catalyst to work without being affected by the cocatalyst.

The heterogenization of a catalyst system affects not only the activities but also the properties of the obtained polymers. In particular, the molecular weights

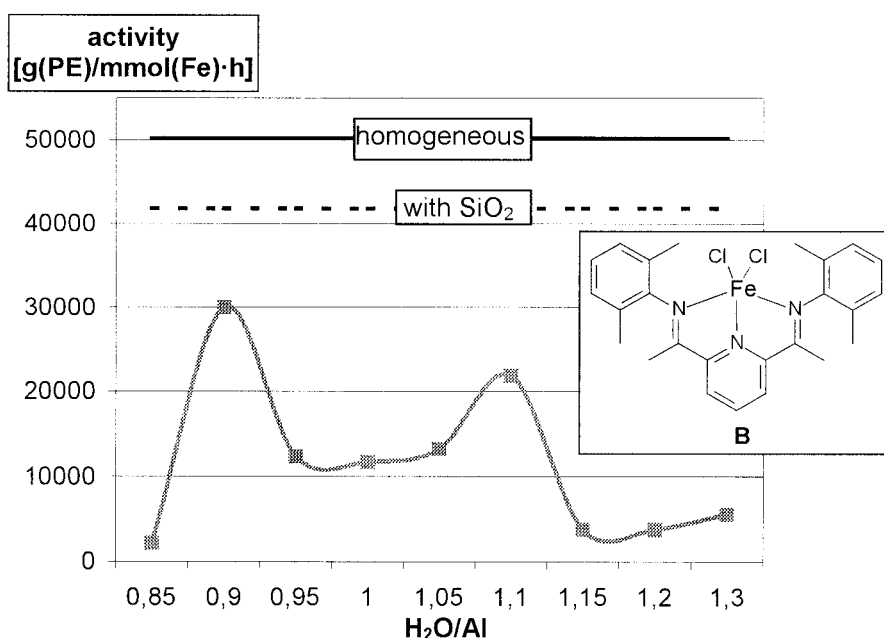


Figure 3 Dependence between the activity and $\text{H}_2\text{O}/\text{Al}$ ratio for **B** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of 60°C , 250 mL of pentane, 1 mL of triisobutylaluminum, $\text{Fe}/\text{Al} = 1/250$, and a time period of 1 h. The maximum activities obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

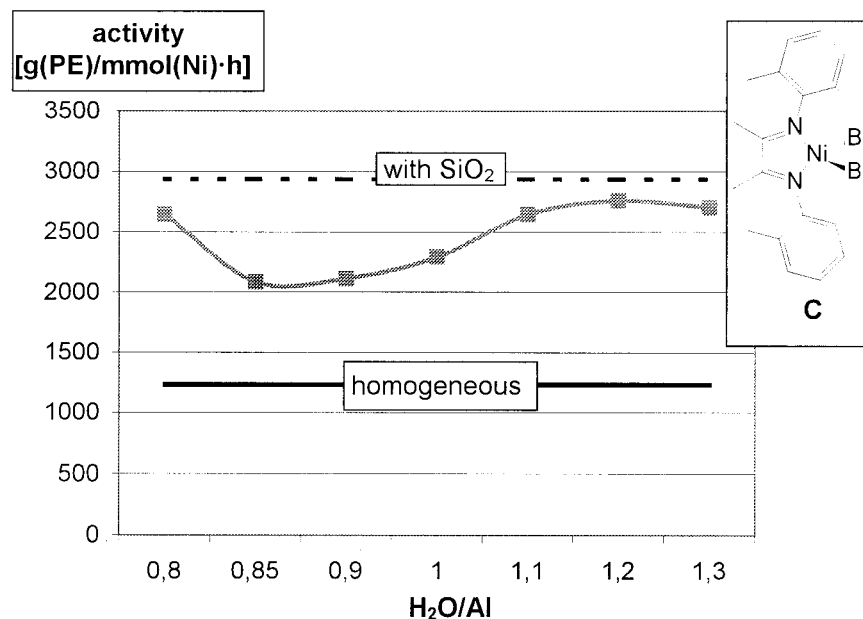


Figure 4 Dependence between the activity and H_2O/Al ratio for **C** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of $60^\circ C$, 250 mL of pentane, 1 mL of triisobutylaluminum, $Ni/Al = 1/250$, and a time period of 1 h. The maximum activities obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

of the polymers can be used as an indicator for the influence of the cocatalyst on the performance of the catalyst. The molecular weight of a polymer results mainly from the polymerization mechanism. Therefore, the molecular weights of the polymer also can be correlated to the composition of the cocatalyst and its ability to activate the catalyst precursor.

In the case of **A**, the catalyst system produced a polymer of comparatively low molecular weight at its maximum activity ($H_2O/Al = 0.90$; Fig. 6).

At this point, a maximum number of zirconocene centers should be activated and should compete for the monomer. The results are low molecular weights because termination reactions such as β -H elimination are also favored. This situation can be compared with the conditions for the homogeneous polymerization and with systems heterogenized on silica. In the region in which the H_2O/Al ratio is lower than 0.90, the catalyst is not activated completely. Therefore, the number of active centers is reduced, and the catalyst

produces higher molecular weights. At H_2O/Al ratios of 0.60 and 0.70, only a few centers are active, and there is an equilibrium reaction between the polymerization steps and the activation step leading to more chain termination reactions and to lower chain lengths. In the region of H_2O/Al ratios greater than 0.90, the increasing oxygen content leads to a deactivation of catalytic centers and to increasing molecular weights.

Catalyst precursor **B** showed a different behavior. The molecular weight of the polymer was high in the region in which the activities also reached their highest values (Fig. 7).

The reason could be slightly different kinetics of the polymerization mechanism between the catalyst precursors **A** and **B**. For **B**, the insertion reaction was the dominating step, whereas for **A**, the coordination of a monomer molecule was decisive. In addition, the molecular weights obtained with the heterogeneous systems were clearly higher than those for the homogeneously produced polymers. The presence of a support material seemed to suppress chain termination reactions and cause higher molecular weights.

For the nickel catalyst **C**, no clear dependence between the molecular weights and cocatalyst composition could be found either as it was observed for the activities (Fig. 8).

The molecular weights were much higher than those obtained in the homogeneous polymerization. This effect was parallel to the observation made for the activities. Just as **B** did, **C** also produced longer polymer chains at higher activities.

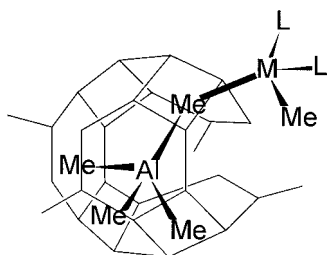
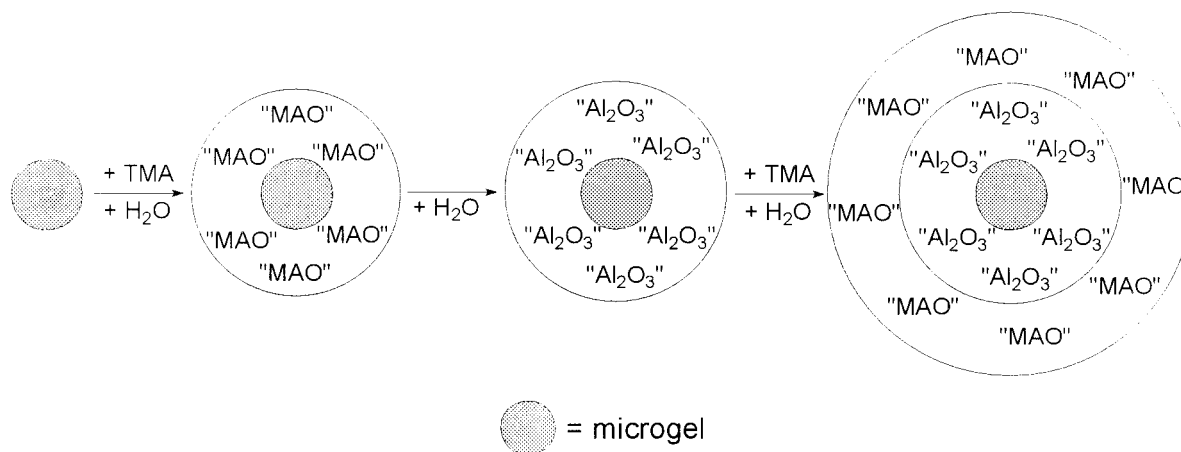


Figure 5 Stabilization of the active species in a transition-metal catalyst ($M = \text{metal}$, $L = \text{ligand}$, and $Me = \text{methyl}$).^{39–43}



Scheme 3 Formation of a second activating layer on the surface of a cocatalyst particle.

CONCLUSIONS

The cocatalysts supported on microgels were able to activate catalyst precursors of different chemical natures. Through variations in the H_2O/Al ratios used for the cocatalyst preparation, the catalyst systems were optimized very easily and adjusted to the individual requirements. The concept of the heterogenization of a catalyst through the support of a cocatalyst was at least successful for the zirconocene derivative **A** and the iron complex **B**. For the Brookhart-type catalyst **C**, reactor fouling could not be avoided because of the differences in the polymerization mechanisms concerning activation and chain propagation. The disadvantages of rather low catalytic activities in

the heterogeneous systems of **A** and **B** were reduced by fine tuning of the cocatalyst composition.

EXPERIMENTAL

All preparations were performed under a purified argon atmosphere with a standard Schlenk technique for the prevention of traces of air or moisture (BTS as a catalyst and molecular sieves were used). All solvents purchased were technical-grade and were purified by distillation over an alloy of sodium and potassium under an argon atmosphere.

The catalyst precursors **A**, **B**, and **C** were synthesized according to the literature.

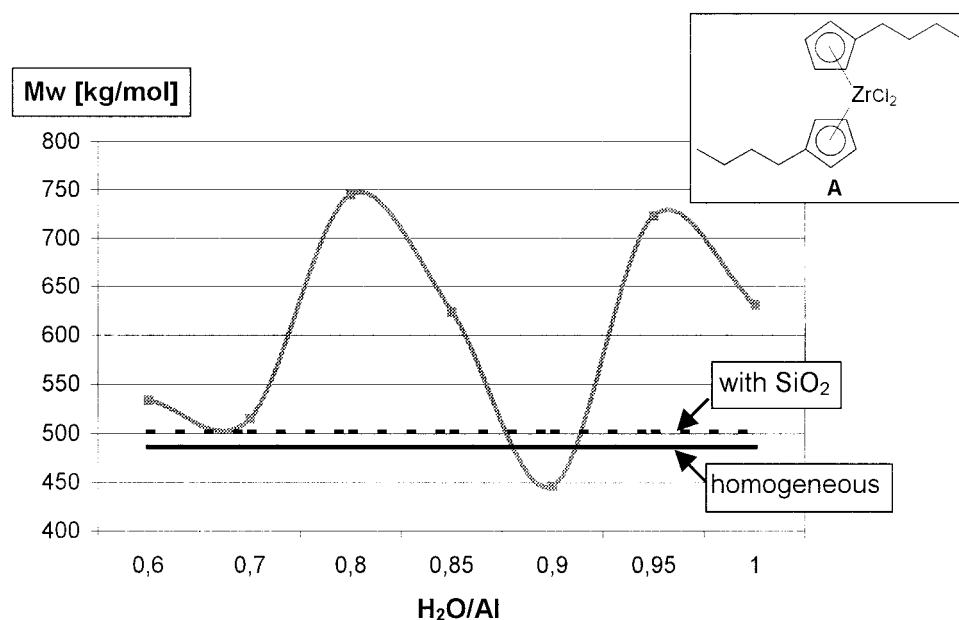


Figure 6 Dependence between the molecular weight of the polymers and the H_2O/Al ratio for **A** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of $60^\circ C$, 250 mL of pentane, 1 mL of triisobutylaluminum, $Zr/Al = 1/250$, and a time period of 1 h. The maximum molecular weights obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

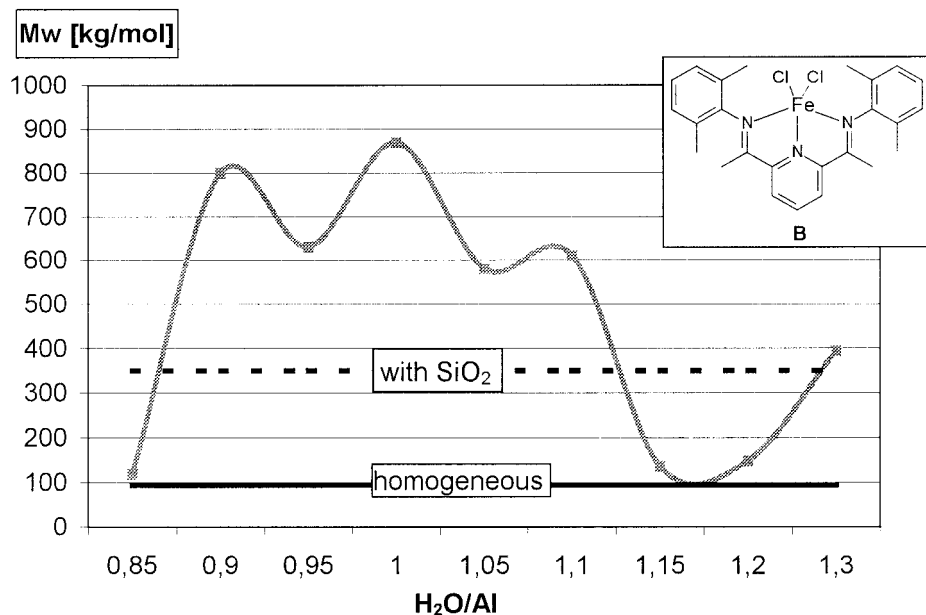


Figure 7 Dependence between the molecular weight of the polymers and the H_2O/Al ratio for **B** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of $60^\circ C$, 250 mL of pentane, 1 mL of triisobutylaluminum, $Fe/Al = 1/250$, and a time period of 1 h. The maximum molecular weights obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

MAO was supplied by Witco GmbH (Bergkamen) as a 30% solution in toluene (average molecular weight = 1100 g/mol, aluminum content = 13.1%, with 3.5% trimethylaluminum).

Molecular weight determinations of PE samples were performed with a Millipore Waters 150 C HT-GPC instrument with refractometric detection (Waters 401 refractive-index detector). The polymer samples

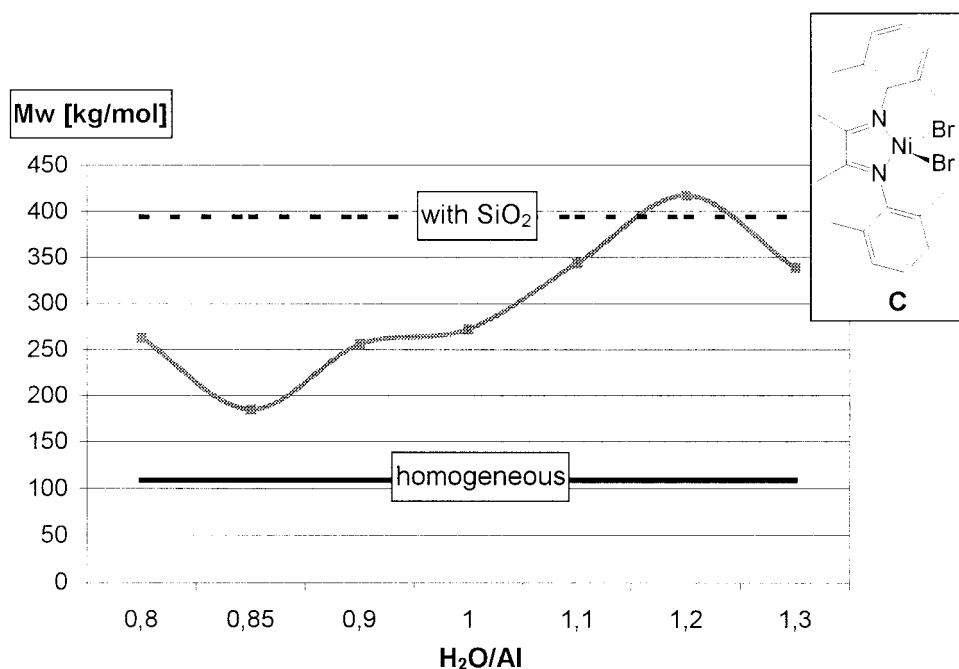


Figure 8 Dependence between the molecular weight of the polymers and the H_2O/Al ratio for **C** with the following polymerization conditions: 10 bar of ethylene pressure, a temperature of $60^\circ C$, 250 mL of pentane, 1 mL of triisobutylaluminum, $Ni/Al = 1/250$, and a time period of 1 h. The maximum molecular weights obtained with the silica-supported catalysts and for the homogeneous case are indicated as lines.

were dissolved in 1,2,4-trichlorobenzene (flow rate = 1 mL/min) and were measured at 150°C.

Synthesis of the heterogeneous catalysts

The support material (microgel or silica; 1.0 g) was dispersed/suspended in 100 mL of toluene. To the dispersion, 30 mL of a 2M TMA solution in toluene was added. 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 the partial hydrolysis of TMA, the catalyst precursor (A, B, or C) was added in the desired ratio. The mixture was stirred for an additional 30 min until a color change indicated the activation of the catalyst precursor. The mixture was filtered over a frit. After filtration, the obtained solid was washed twice with *n*-pentane and dried in vacuo until the weight had stabilized. The yield was 90–95%.

Activation of the homogeneous catalysts with MAO

The corresponding complex (5–10 mg) was suspended in toluene and activated with an excess of MAO (Al/M = 2500/1). The activated catalyst was used for ethylene polymerization within 30 min.

Polymerization of ethylene

The activated complex was added to a 1-L metal autoclave (Büchi, Switzerland) filled with 250 mL of *n*-pentane. The polymerizations were performed under an ethylene pressure of 10 bar (99.98% ethylene, dried over aluminum oxide) and at a temperature of 60°C. After a period of 1 h, the polymerization was stopped by a reduction in the pressure. The remaining polymer was dried in vacuo and weighed.

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