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Heterogeneous catalyst mixtures for the polymerization of ethylene

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Abstract

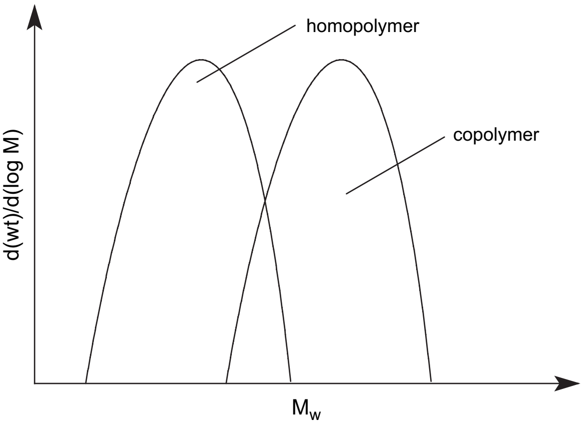
Heterogeneous cocatalysts, catalysts, and catalyst mixtures for the polymerization of ethylene were prepared applying "fumed silica" and mesoporous MCM-41 support materials and zirconocene dichloride, titanocene dichloride, and a bis(arylimino)pyridine iron complex as catalyst precursors. The catalyst mixtures produced polyethylenes which exhibit the properties of two single polymers. Polyethylenes with the desired bimodal molecular weight distributions could be obtained with a series of ternary Zr/Ti/Fe catalysts. The ability of the zirconium and titanium species to copolymerize short-chain 1-olefins produced by the iron centers ("in situ" copolymerization) is useful for the production of copolymers from only one monomer (ethylene).

Keywords: Heterogeneous catalysts; Ethylene polymerization; Polyethylene

1. 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] and references therein). The produced polyolefins have narrow molecular weight distributions due to identical active sites of the catalyst. However, this can be disadvantageous for industrial processings like extrusion or injection moulding. Therefore, a huge number of inorganic and organic compounds have been tested as support materials for catalyst precursors for the heterogeneous polymerization of 1-olefins. Silica gels are the most common supports [27–32], but many other materials like magnesium chloride [33–36], aluminum oxide [37–39], charcoal [40], polypropylene [41], polystyrene [42,43], zeolites [44–48], μ-gels [49–58], starch [59], or even cherry pits [60] were applied. Due to their high surface areas, zeolites, especially mesoporous crystalline materials (e.g. MCM-41), have attracted a lot of attention as support materials in the past few years.

Besides broader molecular weight distributions, regularly distributed branches at the polymer chains can also improve the mechanical properties of polyolefins. Such "linear low density polyethylenes" (LLDPEs) are obtained by copolymerization of ethylene with short-chain 1-olefins. An ideal polyolefin would consist of a low molecular weight homopolymer and a high molecular weight 1-octene/ethylene copolymer (Scheme 1).



Scheme 1. Desired molecular weight distribution of polyolefins for technical processing.

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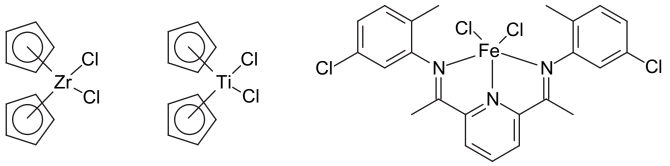
In order to obtain broader molecular weight distributions, cumbersome or costly approaches, like the blending of different resins, are necessary. On the other side, in most cases, it is not possible to obtain the desired multimodal resins by mixing individual mononuclear catalysts (averaging effect). Dinuclear complexes [61–66] proved to be useful catalyst precursors for the synthesis of such materials but their time-consuming synthesis and possible interactions between the active centers made us look for an easier access to polyolefins with the desired properties. A better separation of the active centers of polymerization catalysts may be achieved with heterogeneous catalyst mixtures. Therefore, mononuclear catalyst precursors were activated with heterogeneous cocatalysts. Varying the amount and the type of the applied catalyst precursors, polymers with modified properties should be obtained. Employing precatalysts that are able to copolymerize ethylene with higher 1-olefins, copolymers would be produced “in situ”.

2. Results and discussion

2.1. General remarks

As catalyst precursors, zirconocene dichloride (**I**), titanocene dichloride (**II**), and bis(arylimino)pyridine iron complex (**III**) [67] (Scheme 2) were employed.

While the metallocene complexes **I** and **II** produce polyethylenes with different molecular weights, the iron complex **III** was applied to oligomerize ethylene to give 1-olefins like 1-octene. These oligomers would be consumed by the metallocene complexes producing an ethylene/1-olefin copolymer.



I **II** **III**

Scheme 2. Selected catalyst precursors: zirconocene dichloride (**I**), titanocene dichloride (**II**), bis(arylimino)pyridine iron dichloride complex (**III**).

Due to their high surface areas, zeolites, especially mesoporous crystalline materials (e.g. MCM-41), have been chosen as support materials. These zeolites exhibit crystalline structures and were first described in 1992 by Mobil Research and Development Corporation [68]. Advantageous are their high surface areas (>1000 m^2/g) and uniform hexagonal pores. The pore diameters can be adjusted to 20–100 Å by varying the reaction conditions. Inside and outside the pores, these compounds contain free hydroxyl groups. Depending on the reaction conditions, materials with higher (hs MCM-41) or lower (ls MCM-41) surface areas can be prepared by template synthesis. The surface area of hs MCM-41 was determined to ∼1090 m^2/g while a pore diameter of 34 Å and a pore volume of 0.45 ml/g were found. The surface area of ls MCM-41 was determined as 500 m^2/g.

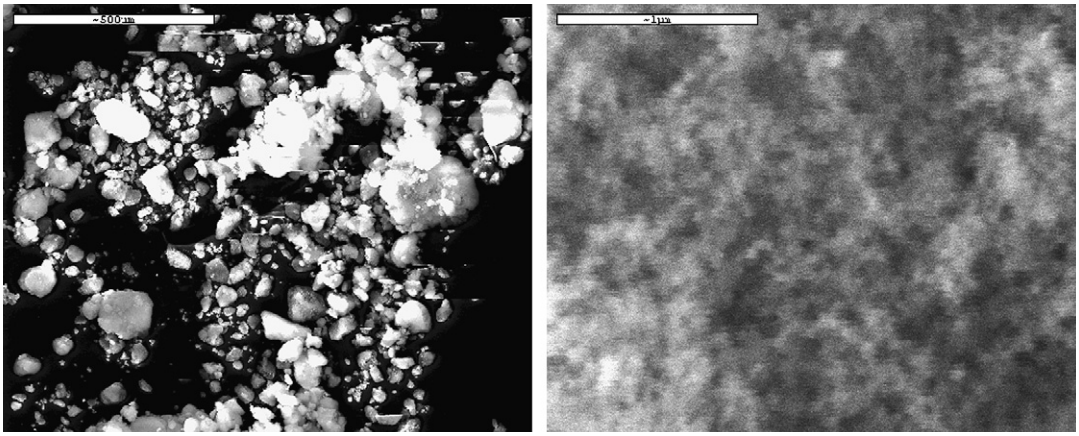
Besides MCM-41, “fumed silica” (Sigma Aldrich, $a = 200\ m^2/g$) and Davison-SiO_2 (Davison 948, calcined) were employed for the synthesis of heterogeneous catalysts. The support materials were characterized by SEM and EDX revealing that “fumed silica” is an amorphous silica gel and consists of irregularly formed particles which can be described as agglomerates of smaller particles with sizes below 50 nm (see Scheme 3).

SEM photographs of hs MCM-41 showed chunkier spherical particles and smaller irregularly formed motes (Scheme 4). At higher resolution, a mixture of differently formed small particles and particles with “worm-like” structures were observed.

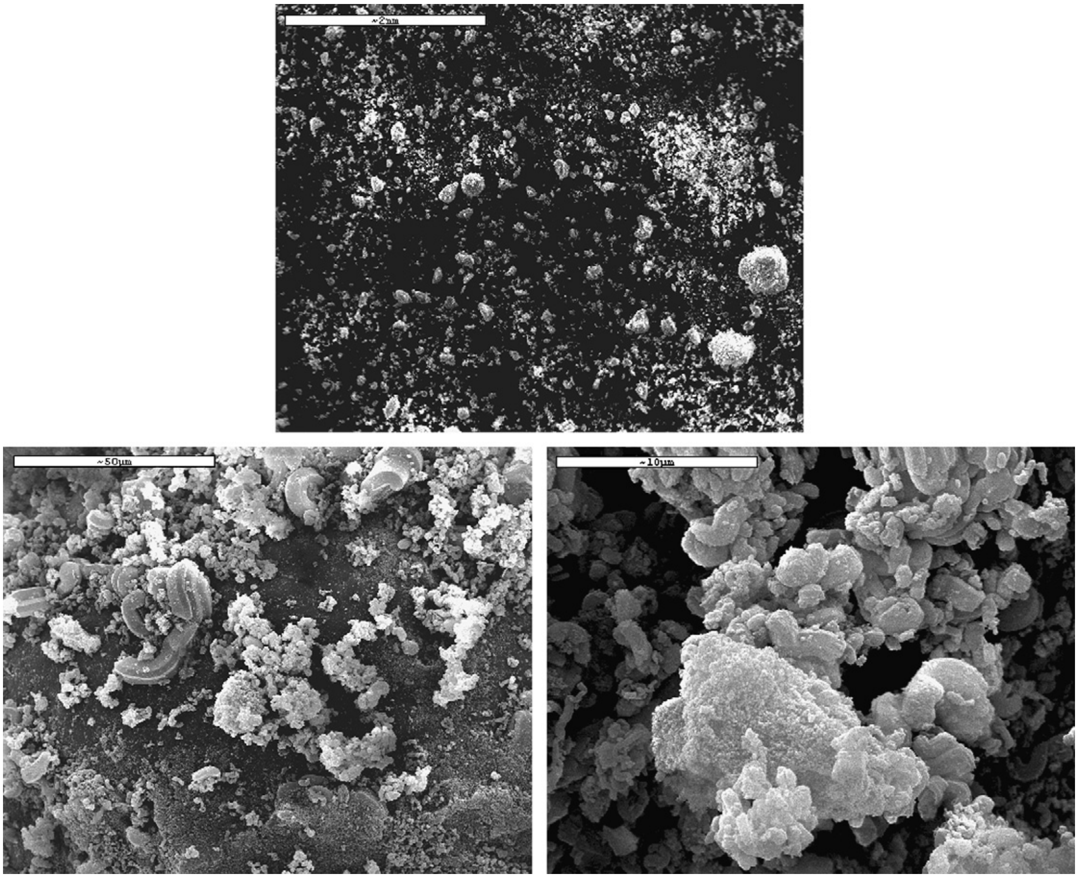
Silicon atoms in MCM-41 can be partially substituted with tetravalent metals like titanium (TiMCM-41) or zirconium (ZrMCM-41) applying $Ti(OBu)_4$ or $Zr(OBu)_4$ as starting materials.

2.2. Synthesis and characterization of the heterogeneous cocatalysts

The heterogeneous cocatalysts were prepared by the “PHT method” [54–57]. Trimethylaluminum is added to a suspension of the support material in toluene. After careful addition of a defined amount of water steam (usually $H_2O:Al \sim 1:1$), partially hydrolyzed trimethylaluminum (PHT) is obtained on the surface of the support material. In contrast to



Scheme 3. SEM photographs of “fumed silica”. Left: scale 500 µm; right: scale 1 µm.



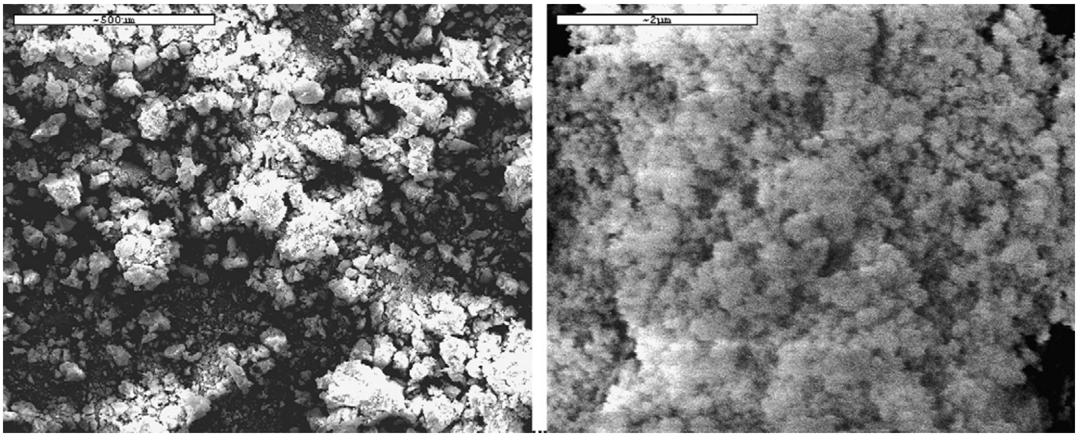
Scheme 4. SEM photographs of hs MCM-41. Top: scale 2 mm; bottom left: scale 50 µm; bottom right: scale 10 µm.

homogeneous systems with dynamic equilibria of aluminum species, supported cocatalysts prepared using the PHT method mainly exhibit cage-like aluminum–oxygen structures which seem to be responsible for an effective activation of catalyst precursors. To the heterogeneous cocatalyst/support system, the catalyst precursor is added. After workup, the heterogeneous catalyst is obtained as a pyrophoric solid.

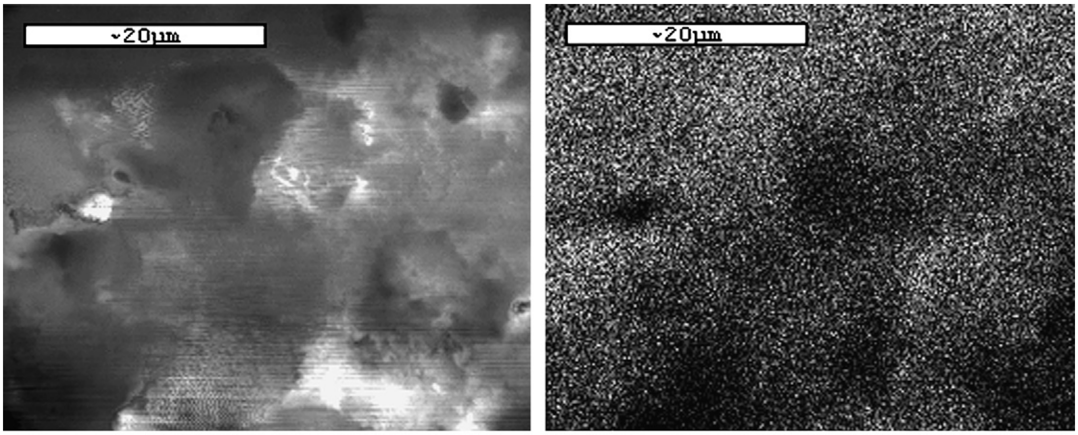
2.2.1. *Cocatalysts prepared from ''fumed silica''*

SEM analyses of the ''fumed silica'' based cocatalyst showed two types of agglomerates. The first type of agglomerates contained fine particles with sizes of 200–300 nm while the second type consisted of smaller particles with sizes around 100 nm. Compared with the support material (particle sizes <50 nm), the heterogeneous cocatalyst exhibits particle sizes which are higher by factors of 2–6 (Scheme 5).

To check whether the support material is equally coated with aluminum species, X-ray element distribution (EDX) analyses were performed providing the following composition: 51.3% oxygen, 16.9% aluminum, and 31.8% silicon (Scheme 6). The particles exhibited distinctively different aluminum and silicon contents.

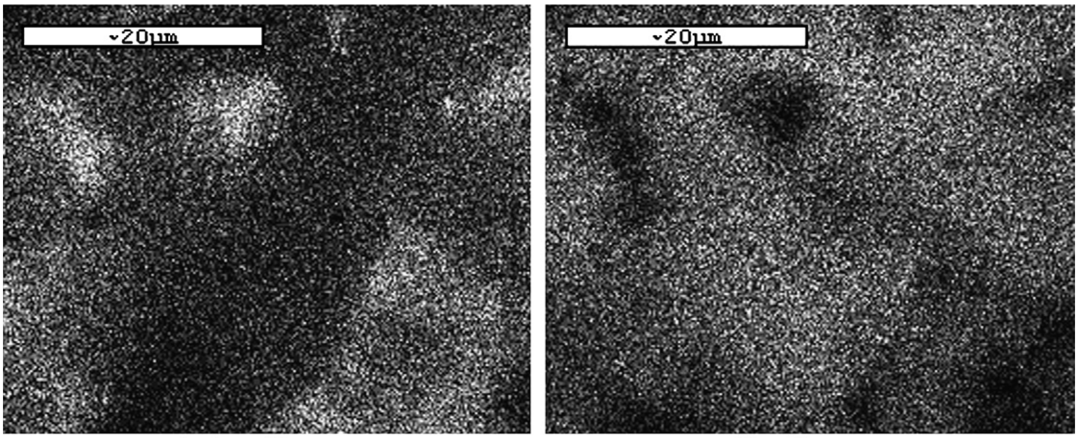


Scheme 5. SEM photographs of the cocatalyst based on ''fumed silica'' (synthesis of the cocatalyst: 2.0 g of fumed silica, $H_2O:Al = 0.9$).



SEM photograph

oxygen X-ray map



aluminum X-ray map

silicon X-ray map

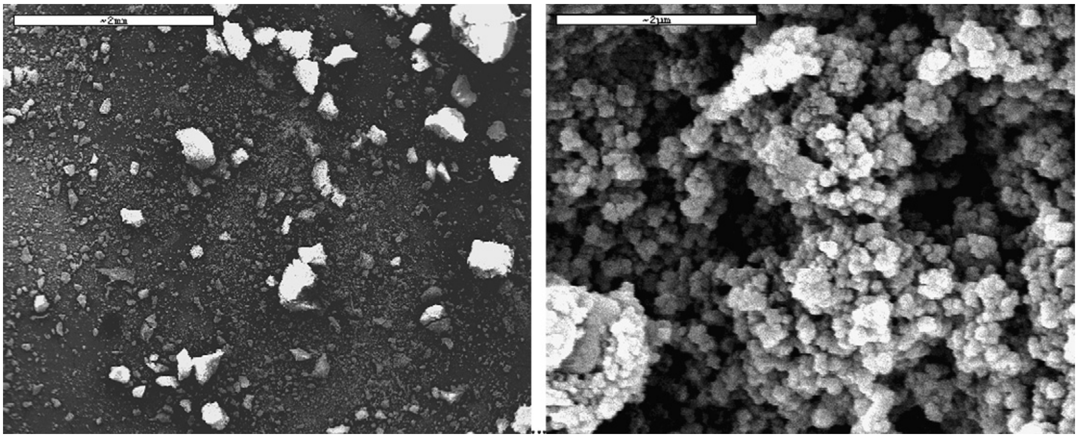
Scheme 6. Element distribution on the cocatalyst surface determined by EDX.

In regions with high aluminum content, the silicon content was low. This result reveals that the support material is not covered uniformly with the cocatalyst.

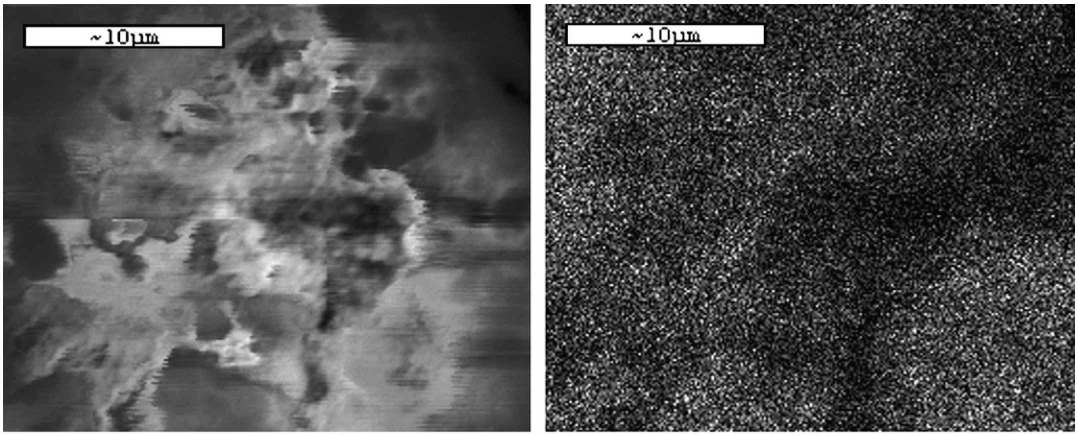
2.2.2. *Cocatalysts prepared from hs MCM-41*

SEM analysis of the hs MCM-41 based cocatalyst showed similar results compared with the ‘‘fumed silica’’ based cocatalyst. Again, two types of particles with diameters of 200–300 nm and 100 nm, respectively, could be observed (Scheme 7).

EDX analyses of the cocatalyst surface gave a composition of 47.6% oxygen, 47.7% aluminum, and 4.5% silicon. Regions with high aluminum content exhibited low silicon contents. Scheme 8 shows that the surface mainly consists of aluminum and oxygen concluding that the support material hs MCM-41 is evenly and nearly completely covered with methylalumoxane. In contrast to the ‘‘fumed silica’’ based cocatalyst, only small regions containing silicon were observed. Therefore, it seems unlikely that an active catalyst species reacts with the support material and is thereby deactivated.

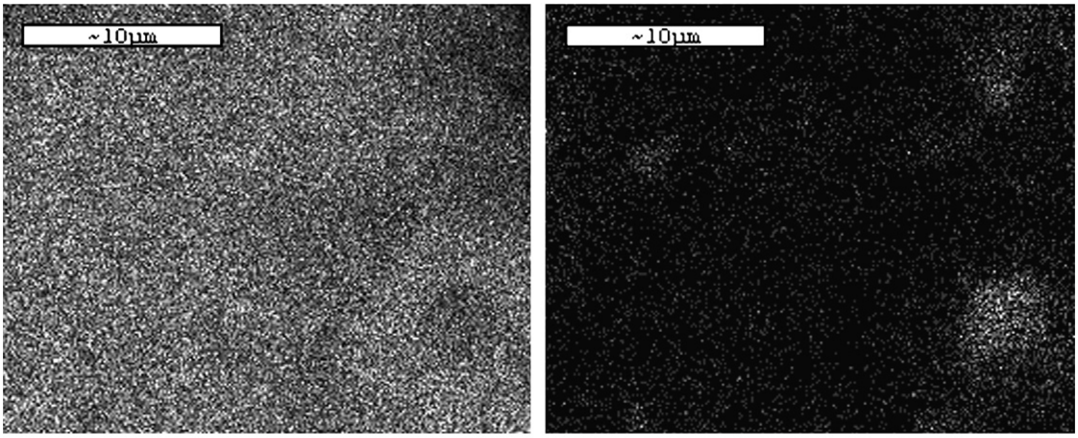


Scheme 7. SEM photograph of the cocatalyst based on hs MCM-41 (synthesis of the cocatalyst: 1.0 g of hs MCM-41, H_2O:Al = 0.9).



SEM photograph

oxygen X-ray map



aluminum X-ray map

silicon X-ray map

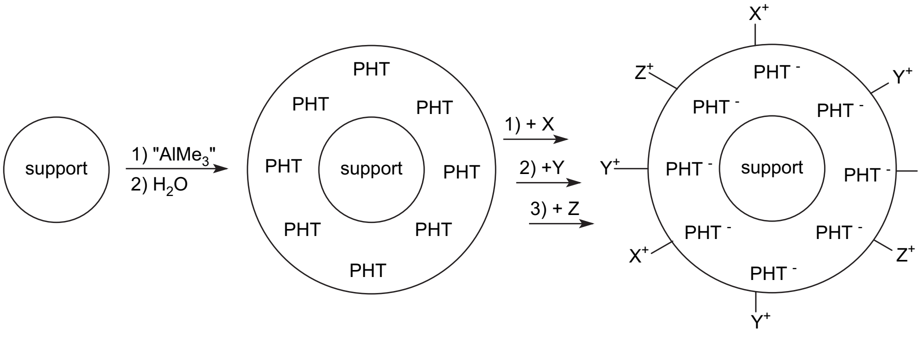
Scheme 8. Element distribution on the hs MCM-41 based cocatalyst surface observed with EDX.

2.3. Synthesis of heterogeneous catalyst mixtures

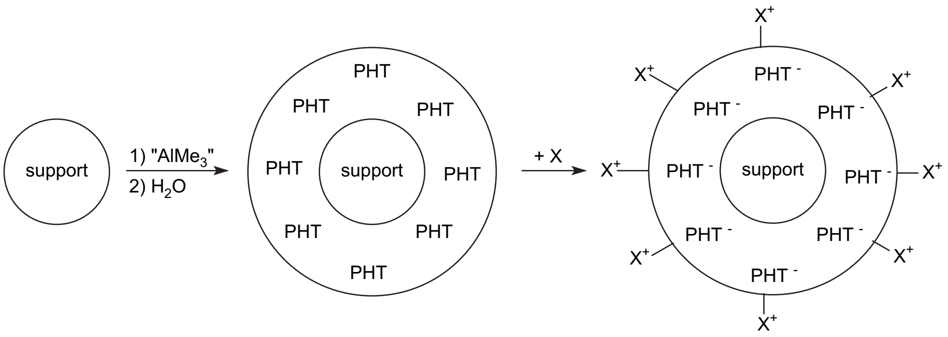
Heterogeneous catalyst mixtures can be principally prepared in two ways. Using method A, different catalyst precursors (X;Y;Z) are added simultaneously to a heterogenized cocatalyst (PHT) (Scheme 9). The influence of different active species on the same cocatalyst anion should be investigated. With this method, interactions of already activated species with subsequently added catalyst precursors could be studied. Since different active species (which can oligomerize or polymerize ethylene) are fixed closely to each other on the surface, this method may be advantageous for "in situ" copolymerization reactions.

Applying method B, the catalyst precursors were separately reacted with the heterogeneous cocatalyst (Scheme 10) providing heterogenized catalysts.

The dried catalyst contains only one active species. Mixtures of such separately heterogenized catalysts were applied for ethylene polymerization experiments. No interactions should occur between active centers except when different catalyst particles are in close contact. However, these catalyst mixtures are not preferred for "in situ" copolymerization



Scheme 9. Synthesis of heterogeneous catalyst mixtures with method A (X,Y,Z = catalyst precursors, X^+,Y^+,Z^+ = catalytically active species).



Scheme 10. Heterogenization and activation of a single catalyst precursor on a heterogenized PHT cocatalyst (X = catalyst precursor, X^+ = active species).

reactions, since the formed 1-olefin must reach a sufficient concentration for an acceptable rate of copolymerization.

2.4. Results of ethylene polymerization reactions

The heterogeneous catalysts and catalyst mixtures were employed for the polymerization of ethylene. The influence of different water:aluminum ratios (used for the PHT preparation) on the polymerization behaviour was investigated.

2.4.1. Catalysts and catalyst mixtures based on "fumed silica"

At first, catalysts based on "fumed silica" were tested in heterogeneous ethylene polymerization reactions. With zirconocene dichloride (**I**) as catalyst precursor, the support:metal ratio was optimized while all other parameters (Al:Zr 200:1; H_2O:Al = 0.9; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 1 h; 10 bar ethylene) were held constant. The highest activity (3365 kg PE/mol Zr h) was observed with a support:metal ratio of 0.15 mmol/g. The molecular weight (M_w) of the resulting polyethylene was determined as 266 700 g/mol. Applying the same reaction conditions, the catalyst system based on Davison-SiO_2 exhibited a distinctively lower polymerization activity (1600 kg PE/mol Zr h). The incompletely aluminum covered support surface still contains Lewis basic centers which can deactivate the active species.

*2.4.1.1. Catalyst mixtures with zirconocene dichloride (**I**) and titanocene dichloride (**II**) as catalyst precursors.* Heterogeneous catalyst mixtures of zirconocene dichloride (**I**) and titanocene dichloride (**II**) were prepared using methods A and B. The polymerization results were compared with the results obtained for the single components and the influence of different zirconium:titanium ratios was investigated. Interestingly, mixtures prepared using method A (Zr:Ti > 1, see Table 1) showed higher activities than both heterogenized single components. This behaviour can only be explained with interactions between the active species. As expected, a nearly additive behaviour in terms of the single components was observed for mixtures prepared using method B. Since catalysts with an enhanced polymerization activity are preferred, method A seemed to be the better choice for these binary catalyst systems. Table 1 shows the polymerization results for a series of catalyst mixtures including the results for the polyethylenes obtained with the single components.

Titanocene dichloride (**II**) supported on "fumed silica" showed the lowest polymerization activity in the series (465 kg PE/mol M h), while the catalyst with solely supported zirconocene dichloride (**I**) provided polyethylene with an activity of 3335 kg PE/mol M h. Especially mixtures with Zr:Ti ratios > 1:1 gave higher activities than the single zirconocene catalyst. The molecular weights (M_ws) of the obtained polyethylenes range from 261 000 g/mol (Zr:Ti = 1:0) to 527 600 g/mol (Zr:Ti = 0:1) while for the mixtures, the M_w values do not exceed these limits (except for Zr:Ti = 100:1).

2.4.1.2. Ternary catalyst mixtures. Due to its attractive mechanical properties, "linear low density polyethylene" (LLDPE) has gained increased attention in the past few years. The production process requires an external addition of comonomers like 1-hexene or 1-octene to the polymerization reactor. Appropriately substituted bis(arylimino)pyridine iron complexes [69,70] proved to be very active for the oligomerization of ethylene to give short-chain 1-olefins in both homogeneous and heterogeneous media. Heterogeneous mixtures of oligomerization catalysts (especially bis(arylimino)pyridine iron complexes) and polymerization catalysts with the ability to copolymerize ethylene and short-chain 1-olefins (especially

Table 1
Results of ethylene polymerization reactions with heterogenized mixtures of zirconocene dichloride (**I**) and titanocene dichloride (**II**) with regard to the Zr:Ti ratio

Zr:Ti ratio	Activity [kg PE/mol M h]	M_n [g/mol]	M_w [g/mol]	PD
0:1	465	152 360	527 600	3.46
1:9	2400	108 900	345 820	3.18
2:8	3375	102 140	300 980	2.95
3:7	3230	106 720	323 300	3.03
4:6	3470	106 230	308 630	2.91
1:1	2980	111 760	378 170	3.38
6:4	3445	99 270	254 650	2.57
7:3	4710	98 920	278 060	2.81
8:2	4365	110 610	297 920	2.69
9:1	4590	114 000	288 790	2.53
100:1	4250	75 200	195 650	2.60
1:0	3365	109 590	266 700	2.38

Polymerization conditions: method A; Al:M = 200:1; H_2O:Al = 1.0; "fumed silica" with *n*(metal):*m*(support) = 0.15 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

metallocene complexes) would avoid the external addition of the comonomers since they were produced and consumed ''in situ'' (''just in time delivery''). Therefore, ternary mixtures of heterogenized catalysts were prepared and investigated in terms of their ethylene polymerization behaviour.

Bis(arylimino)pyridine iron dichloride complex (**III**) produced 1-olefins with an activity of 6300 kg/mol Fe h in homogeneous media when activated with MAO (Al:Fe = 200:1). The obtained mixture also contained low molecular weight polyethylene (8.3 wt%). After heterogenization on ''fumed silica'' (PHT, H_2O:Al = 0.9:1), both the activity and the polymer fraction increased by a factor of 2 (11 600 kg/mol Fe h; 13.7 wt%; see Table 2). The highest activity for this catalyst system was obtained when a water:aluminum ratio of 1:1 was applied. A tremendous increase (53 400 kg/mol Fe h) was observed under these conditions. An analysis of the product composition revealed a polymer fraction of 19.7 wt%. The mixture of 1-olefins could be nicely characterized by GC/MS applying the Schulz–Flory statistical approach [71,72].

The Schulz–Flory coefficient α can be calculated from the GC integrals as the quotient of the molar amounts of two subsequent oligomer fractions:

$$\alpha = \frac{n(C_{n+2})}{n(C_n)}$$

(where n is the number of carbon atoms of the olefin molecule).

A smaller value of the Schulz–Flory coefficient implicates a higher percentage of short-chain olefins in the product composition. As can be seen from Table 2, the Schulz–Flory coefficient rises along with the polymer fraction from the homogeneous system to the heterogeneous systems.

For testing the ability of the active metallocene species to copolymerize ethylene with higher 1-olefins, the binary system **I**/**II**/PHT (with Zr:Ti = 1:1) was prepared according to method A. An oligomer mixture with known composition ($\alpha = 0.81$) was added to the polymerization reactor. GC analyses of the oligomer fractions before and after the (co)polymerization reaction revealed that 1-hexene was nearly completely consumed during the copolymerization reaction (Scheme 11) while other hexene isomers remained in the reaction solution. Also, the contents of 1-octene and 1-decene decreased but the copolymerization rates of ethylene with these higher 1-olefins are distinctively lower compared with the consumption of 1-hexene.

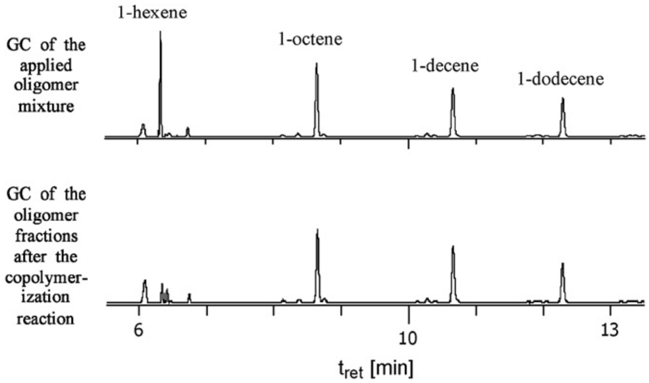
DSC analyses of the resulting polymers also gave proof for the copolymerization. The melting point of the polyethylene obtained from the copolymerization reaction was determined as 131.2 °C which is 5.3 K lower compared with the melting point of the homopolymer (Scheme 12).

Table 2
Results of ethylene polymerization reactions with the catalyst precursor **III**

H_2O:Al	Activity [kg PE/mol M h]	M_n [g/mol]	M_w [g/mol]	PD	wt% PE	Schulz–Flory coefficient α
Homogeneous[a]	6300	1190	12 360	10.41	8.3	0.74
0.9[b]	11 630	1240	6840	5.53	13.7	0.78
1.0[b]	53 400	1430	11 800	8.26	19.7	0.81

[a] Homogeneous: activation with MAO (Al:Fe = 200).

[b] Heterogeneous: Al:Fe = 200:1; ''fumed silica'' with n(Fe):m(support) = 0.15 mmol/g; 250 ml n-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

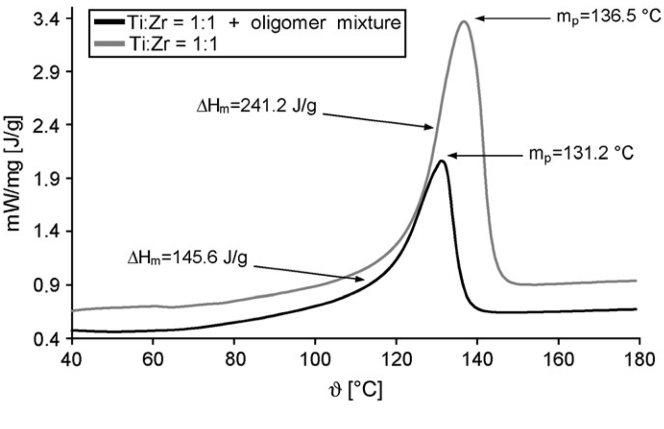


Scheme 11. GC spectra of the oligomer mixtures before and after the copolymerization reaction. Polymerization conditions: catalyst precursors **I** and **II** (Zr:Ti = 1:1); method A: Al:M = 200:1; H_2O:Al = 1.0; ''fumed silica'' with n(metal):m(support) = 0.15 mmol/g; 250 ml n-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene; 21.75 g of oligomer mixture with $\alpha = 0.81$.

Due to the short-chain branches, the crystallization of the macromolecules is hindered and the melting enthalpy (ΔH_m) of the copolymer is quite low (145.6 J/g) compared with the melting enthalpy of the homopolymer (241.2 J/g).

The polymerization activities of ternary catalyst systems prepared using both methods A and B (**I**/**II**/**III**/PHT) are surprisingly low (see Table 3), probably due to interactions of the different catalyst species. Especially catalysts with higher contents of the iron precursor **III** should exhibit considerably higher activities. Apparently, the iron species seem to be blocked by the metallocene species.

Compared with the activity of the binary Zr/Ti catalyst (Table 3, row 1), the activities of the ternary catalysts (at Zr:Ti:Fe ratios of 16:16:1 and 8:8:1) prepared by method A increase but decrease for catalysts synthesized by method B. However, the catalyst system with Zr:Ti:Fe = 4:4:1 prepared by method B was considerably more active indicating a diminished rate of deactivation due to the separate heterogenization of the catalyst precursors. As can be expected, the polymer molecular weights (M_ws) of polyethylenes decrease



Scheme 12. DSC curves of polyethylenes obtained from homopolymerization (grey line) and copolymerization (black line).

Table 3
Ethylene polymerization data of ternary Zr/Ti/Fe/PHT catalyst mixtures

Zr:Ti: Fe	Method	Activity [kg PE/mol M h]	wt% PE	wt% oligomer	M_n [g/mol]	M_w [g/mol]	Modality[a]	PD	ΔH_m [J/g]	m_p [°C]	Crystallinity α
1:1:0	A	1425	100.0	0.0	104 210	419 770	s	4.028	139.0	135.7	0.479
16:16:1	A	1555	84.9	15.1	108 740	306 025	m	2.814	151.8	135.0	0.523
16:16:1	B	1387	72.6	27.4	6730	197 600	b	29.357	88.5	125.4	0.496
8:8:1	A	2174	93.3	6.7	118 040	310 310	m	2.629	150.2	134.5	0.518
8:8:1	B	1357	51.9	48.1	3350	111 410	b	33.227	78.0	124.1	0.723
5:5:1	A	1091	96.0	4.0	89 810	269 390	m	3.000	131.6	131.1	0.454
4:4:1	A	1461	82.2	17.8	79 930	247 815	m	3.100	112.6	130.0	0.388
4:4:1	B	2337	30.7	69.3	2030	69 510	b	34.172	143.3	122.0	0.479
3:3:1	A	496	53.9	46.1	9370	226 540	b	24.168	112.3	129.4	0.387
2:2:1	A	2293	84.9	15.1	12 090	172 440	b	14.261	109.0	125.7	0.376
1:1:1	A	1536	58.0	42.0	3850	89 450	b	23.271	95.8	124.1	0.330
1:1:2	A	1388	43.0	57.0	9070	167 800	b	18.495	113.8	125.5	0.479
0:0:1	–	11 626	13.7	86.3	1240	6840	s	5.525	209.6	123.6	0.305

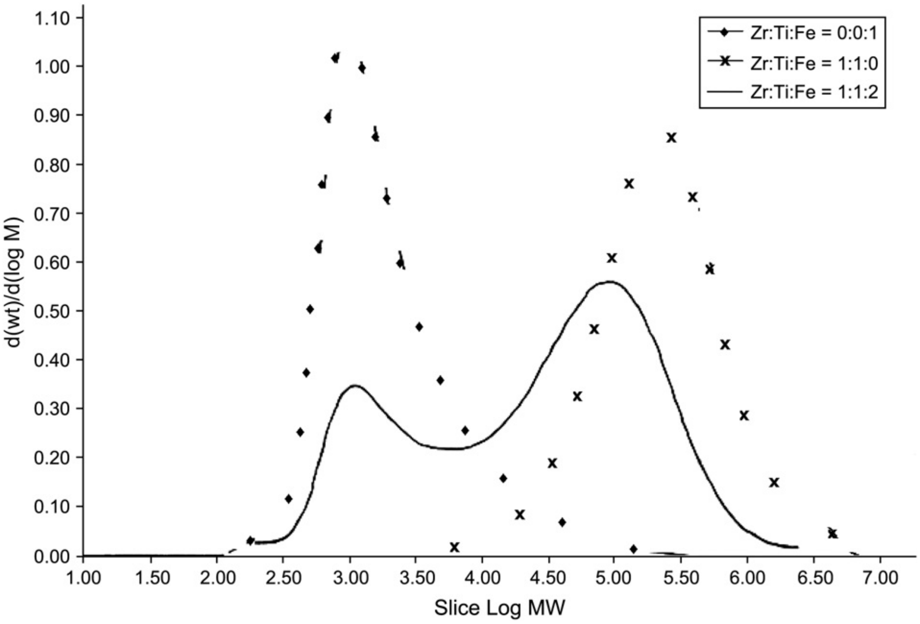
Polymerization conditions: Al:M = 200:1; H_2O:Al = 0.9; "fumed silica" with n(metal):m(support) = 0.15 mmol/g; 250 ml n-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

[a] s: shoulder; m: monomodal; b: bimodal.

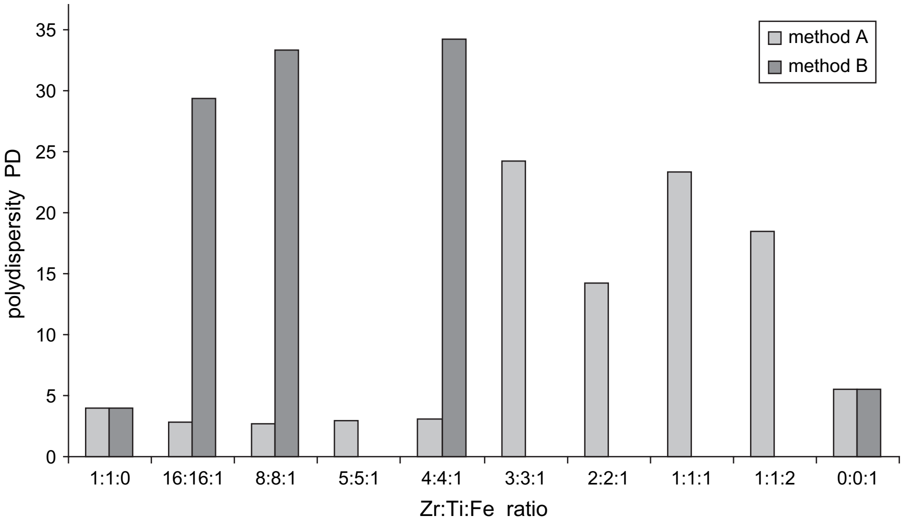
with an increasing content of the iron containing catalyst precursor **III**. In many cases, bimodal molecular weight distributions were obtained (Scheme 13) in GPC analyses. The lower molecular weight fractions resemble to the polymer obtained with **III**/PHT while the higher molecular weight fractions show peak molecular weights that are somewhat lower compared with the value found for **I**/**II**/PHT. These lower molecular weights may indicate branched polyethylenes.

Due to reduced interactions of the active centers, polyethylenes prepared using method B catalysts exhibit significantly lower molecular weights (M_ws). Since the iron centers are not blocked they show enhanced productivities towards 1-olefins and low molecular weight polyethylenes. Due to the greater distance of the iron centers to the copolymerizing titanium and zirconium centers, the copolymerization rate is drastically reduced leading to bimodal molecular weight distributions and remarkably high polydispersity values even for catalysts with low iron content (see Table 3 and Scheme 14). In the case of polyethylenes obtained with method A catalysts, most of the formed short-chain 1-olefins are immediately consumed (=copolymerized) by the nearby titanium and zirconium centers resulting in smaller polydispersities and constant low oligomer fractions of the product compositions. Higher polydispersity values were only observed when the iron content exceeded a Zr:Ti:Fe ratio of 3:3:1.

While the method A catalysts produced polyethylenes with monomodal MWDs (from ratios Zr:Ti:Fe = 16:16:1 up to 4:4:1), the polymers obtained with the corresponding method B catalysts exhibited bimodal GPC curves (see Scheme 15).



Scheme 13. GPC curves of polyethylenes obtained with the iron catalyst **III**/PHT (*rhombs*), the binary Zr/Ti catalyst **I**/**II**/PHT (Zr:Ti = 1:1; method A; *crosses*), and the ternary catalyst **I**/**II**/**III**/PHT (Zr:Ti:Fe = 1:1:2; method A; *plain*).

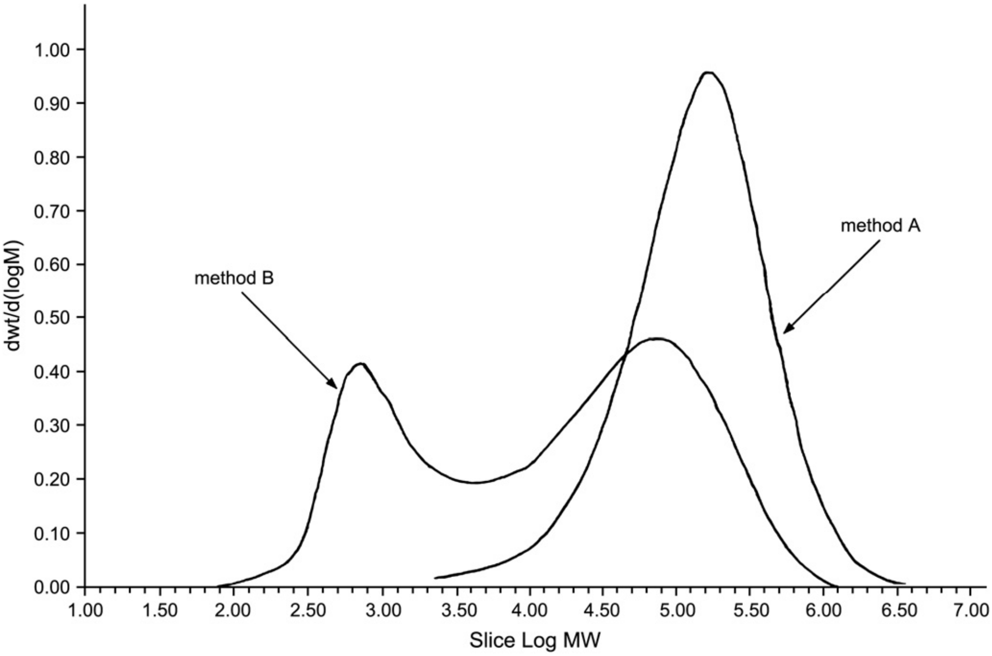


Scheme 14. Polydispersity values of polyethylenes prepared using ternary catalysts.

Analogous to the molecular weights, the melting points of method B polymers are considerably lower (∼ 10 K) than the values found for method A polymers.

2.4.1.3. Influence of the polymerization temperature on the polymerization activity and the product composition. Polymerization reactions were performed at 40 °C, 60 °C, and 80 °C to investigate the influence of the reaction temperature on both activities and product compositions. Table 4 gives an overview of the results.

While the activity of the titanium catalyst **II**/PHT decreases with increasing polymerization temperature, the single zirconium and iron catalysts **I** and **III** and the ternary system **I**/**II**/**III**/PHT exhibited their best activities at 60 °C. For the binary Zr/Ti catalyst showing its highest activity at 40 °C, only a slight decrease in the activity was observed at elevated temperatures. For the three single catalysts **I**/PHT, **II**/PHT, and **III**/PHT, as well as for the binary Zr/Ti system and the ternary Zr/Ti/Fe catalyst, the molecular weights (M_ws) of the produced polyethylenes drop with increasing reaction temperature due to an increased rate of β-hydrogen elimination reactions. The polydispersities of the zirconium catalyzed polymer remained nearly constant at the investigated reaction temperatures while for **II**/PHT a significant increase in the PD was observed. An additive behaviour of the PD can be noted for the binary Zr/Ti system. Analyses of the polyethylenes produced with the ternary catalyst revealed that the polymer fraction increases at elevated reaction temperatures along with the Schulz–Flory coefficient



Scheme 15. GPC curves of polyethylenes produced with a method A catalyst and a method B catalyst applying the same Zr:Ti:Fe ratio (Zr:Ti:Fe = 4:4:1, Al:M = 200:1, H_2O:Al = 0.9, n(metal)/m(support) = 0.15 mmol/g).

Table 4
Ethylene polymerization results for heterogeneous single, binary, and ternary catalyst systems based on "fumed silica" at different reaction temperatures

Precursor(s) (ratio)	Temperature [°C]	Activity [kg PE/mol M h]	M_n [g/mol]	M_w [g/mol]	Modality[a]	wt% PE	wt% oligomer	PD	Schulz–Flory coefficient α
I	40	2420	13 1040	314 490	m	100	0	2.400	–
I	60	3340	109 590	261 220	m	100	0	2.384	–
I	80	1600	66 520	162 120	m	100	0	2.437	–
II	40	760	307 685	866 700	m	100	0	2.817	–
II	60	465	152 360	527 600	s	100	0	3.463	–
II	80	150	31 620	214 480	s	100	0	6.783	–
III	40	47 485	1260	23 240	s	14.6	85.4	18.459	0.812
III	60	53 380	1430	11 795	s	19.7	80.3	8.257	0.809
III	80	20 555	1120	8290	s	17.1	82.9	7.395	0.792
I/II (1:1)	40	3250	163 900	468 350	m	100	0	2.857	–
I/II (1:1)	60	2980	111 760	378 170	s	100	0	3.384	–
I/II (1:1)	80	2740	61 090	219 460	s	100	0	3.592	–
I/II/III (4:4:1)	40	2355	109 000	274 340	m	84.5	15.5	2.517	0.821
I/II/III (4:4:1)	60	2920	77 760	238 350	m	91.6	8.4	3.065	0.82
I/II/III (4:4:1)	80	1880	61 790	186 430	m	96.5	3.5	3.017	0.831

Polymerization conditions: method A; Al:M = 200:1; H_2O:Al = 1.0; *n*(metal):*m*(support) = 0.15 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

[a] s: shoulder; m: monomodal; b: bimodal.

α. Since α usually drops at higher polymerization temperatures, this result may be explained with an enhanced copolymerization rate of the zirconium and titanium centers. Due to the fact that the iron species preferably produced 1-olefins with shorter chain lengths at elevated temperatures, the percentage of higher oligomers in the reaction solution is reduced. These short-chain 1-olefins are favored by the zirconium and titanium centers for the copolymerization with ethylene and are, therefore, removed from the reaction solution.

2.4.2. Catalysts and catalyst mixtures based on MCM-41 supports

Analogous to the "fumed silica" based catalysts, heterogeneous catalysts based on mesoporous MCM-41 compounds were tested for the polymerization of ethylene.

*2.4.2.1. Catalysts and catalyst mixtures with zirconocene dichloride (**I**) and titanocene dichloride (**II**) as catalyst precursors.* Five mesoporous compounds (ls MCM-41, hs MCM-41, TiMCM-41, ZrMCM-41, SiO_2 prepared from sodium metasilicate) were investigated towards their properties as support materials for catalyst precursors. For comparison with the "fumed silica" based catalysts, single catalysts and binary catalyst mixtures were prepared from these mesoporous materials according to method A using zirconocene dichloride (**I**) and titanocene dichloride (**II**) as the catalyst precursors (see Tables 5 and 6). Analogous to the "fumed silica" based catalysts, the metal/support ratio was optimized. For all the MCM based catalysts, the highest polymerization activities were obtained at a ratio of *n* (metal)/*m* (support) = 0.3 mmol/g.

The binary system based on hs MCM-41 showed the highest activity among the five tested supported catalysts. The activity of the ls MCM-41 based catalyst mixture is marginally lower while for the binary catalysts based on the zirconium and titanium doped MCMs the activities decrease considerably. Probably due to its low cross-linking and, therefore, high content of free hydroxyl groups, the silica based catalyst mixture exhibited the lowest polymerization activity in this series. The resulting lower surface prevents a complete heterogenization of the cocatalyst while for ls MCM-41 and hs MCM-41 a nearly complete heterogenization was achieved. Interestingly, higher polymerization activities were observed for the binary catalysts than for the single catalysts for most of the support materials revealing the positive effect of the neighbourhood of two different active species. The undoped MCM-41 based catalyst mixtures produced higher molecular weight polyethylenes compared with their doped analogues possibly due to the more regular catalyst surface. The polydispersities remain nearly constant for the binary catalysts while for some of the single catalysts somewhat higher values were found.

Since the hs MCM-41 based catalysts exhibited the highest polymerization activities, all further experiments were performed with this well-defined support material. As described

Table 5
Ethylene polymerization activities of **I**/PHT, **II**/PHT, and **I**/**II**/PHT depending on the support material

Support material	Catalyst precursor(s)	Activity [kg PE/ mol M h]	M_n [g/mol]	M_w [g/mol]	Modality[a]	PD
hs MCM-41	**I/II**	4360	135 800	438 040	s	3.226
hs MCM-41	**I**	2410	208 520	801 510	b	3.843
hs MCM-41	**II**	810	107 395	231 650	m	2.160
ls MCM-41	**I/II**	3955	136 060	386 470	s	2.840
ZrMCM-41	**I/II**	2160	101 170	325 660	m	3.219
ZrMCM-41	**I**	3870	82 890	213 300	m	2.573
ZrMCM-41	**II**	915	147 545	567 690	s	3.848
TiMCM-41	**I/II**	2580	121 360	370 460	m	3.053
TiMCM-41	**I**	2160	102 080	321 890	m	3.153
TiMCM-41	**II**	710	175 000	663 730	s	3.793
Silica	**I/II**	1110	–	–	–	–

Polymerization conditions: method A; Zr:Ti = 1.5:1 (in mixtures); Al:M = 200:1; H_2O:Al = 0.9; *n*(metal):*m*(support) = 0.3 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

[a] s: shoulder; m: monomodal; b: bimodal.

Table 6
Results of ethylene polymerization reactions with heterogenized mixtures of zirconocene dichloride (**I**) and titanocene dichloride (**II**) with regard to the Zr:Ti ratio

Zr:Ti ratio	Activity [kg PE/mol M h]	M_n [g/mol]	M_w [g/mol]	PD
0:1	810	107 395	231 650	2.157
1:20	1840	–	–	–
1:10	1360	–	–	–
1:5	2260	–	–	–
1:2.5	1970	–	–	–
1:1	2130	94 780	267 330	2.821
1.5:1	4360	135 800	438 040	3.226
2.5:1	2550	–	–	–
5:1	1590	–	–	–
10:1	210	–	–	–
20:1	1745	–	–	–
1:0	2410	208 520	801 310	3.843

Polymerization conditions: method A; Al:M = 200:1; H_2O:Al = 0.9; hs MCM-41 with *n*(metal):*m*(support) = 0.3 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

for the ‘‘fumed silica’’ based catalysts, the dependence of the polymerization activities on the zirconium/titanium ratio was investigated for hs MCM-41 based binary catalysts.

Catalyst mixtures containing similar amounts of the titanium and zirconium precursors proved to be most active for ethylene polymerization. On the other hand, catalysts with low or high zirconium/titanium ratios exhibited somewhat lower activities.

2.4.2.2. Ternary catalyst mixtures based on hs MCM-41. As described for the ‘‘fumed silica’’ based catalysts, heterogeneous ternary catalyst mixtures based on hs MCM-41 were prepared by both methods A and B and investigated towards their behaviour in ethylene polymerization reactions. Different zirconium/titanium/iron ratios were used for the synthesis of these ternary **I**/**II**/**III**/PHT catalysts. The polymerization results are collected in Table 7.

Besides polyethylene, all ternary catalysts also produced oligomeric products. The polymerization activities increased with higher iron contents of the catalyst. This increase in the activity is more obvious for method A catalysts. However, due to the rather low activities of the zirconium and titanium species, the remarkable activity of 26 540 kg PE/mol M h of the single iron catalyst was never reached when ternary catalysts were applied. Compared with the activities of the ‘‘fumed silica’’ based catalysts, the analogous hs MCM based systems are slightly more active indicating the positive effect of the more regular catalyst surface. As expected, the binary **I**/**II**/PHT catalyst produced the polyethylene with the highest molecular weight in this series. Catalysts with higher iron contents lead to polyethylenes with considerably lower molecular weights (M_ws). Due to the high activities of the iron species, this decrease in the molecular weights was more distinct for method A catalysts since the zirconium and titanium centers cannot incorporate the increased amount of short-chain 1-olefins. All polyethylenes produced with the ternary catalysts exhibited high polydispersity values ($17 < \mathrm{PD} < 35$). While for polyethylenes produced with low iron containing catalysts only a shoulder was observed in the molecular weight distribution, bimodal MWDs were obtained for polyethylenes prepared from catalysts with similar zirconium/titanium/iron contents. The investigation of the product compositions revealed that the oligomer contents increased continuously for the more iron rich catalysts. In contrast to the ‘‘fumed silica’’ based systems, ternary method B catalysts based on hs MCM-41 gave oligomer/polymer mixtures with distinctively higher shares in polymer than the corresponding method A catalysts. Since the activities of the method B catalysts do not vary dramatically in this series even for higher iron contents, the structures of the catalytically active species on the catalyst surface may be different. The tubular structure of MCM-41 materials can allow the diffusion of short-chain olefins which are therefore removed from the reaction mixtures leading to lower comonomer incorporation rates for the zirconium and titanium centers.

2.4.2.3. Influence of the polymerization temperature on the polymerization activity and the product composition. As described for the ‘‘fumed silica’’ based catalysts, polymerization reactions were performed at 40 °C, 60 °C, and 80 °C to investigate the influence of the reaction temperature on both activities and product compositions of hs MCM-41 based catalysts. Polymerization data are collected in Table 8.

Similar to the ‘‘fumed silica’’ based systems, the highest activities were observed at 60 °C (for single, binary, and

Table 7
Ethylene polymerization data of ternary **I**/**II**/**III**/PHT catalyst mixtures

Zr:Ti:Fe	Method	Activity [kg PE/mol M h]	wt% PE	wt% oligomer	M_n [g/mol]	M_w [g/mol]	Modality[a]	PD
1:1:0	A	2130	100	0	94 780	267 330	m	2.821
16:16:1	A	2520	40.4	59.6	1960	42 080	s	21.515
16:16:1	B	4440	74.4	25.6	3330	118 050	s	35.498
8:8:1	A	5640	34.1	65.9	1860	41 370	s	22.255
8:8:1	B	3670	54.1	45.9	3010	86 740	b	28.783
4:4:1	A	3220	37.1	62.9	3860	104 910	s	27.173
4:4:1	B	5100	34.8	65.2	2260	69 170	b	30.591
1:1:1	A	11 120	27.0	73.0	1345	23 240	b	17.278
1:1:1	B	5190	34.6	65.4	1560	42 890	b	27.472
0:0:1	–	26 540	23.3	76.7	1100	39 125	s	8.796

Polymerization conditions: Al:M = 200:1; H_2O:Al = 0.9; hs MCM-41 with *n*(metal):*m*(support) = 0.3 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

[a] s: shoulder; m: monomodal; b: bimodal.

Table 8
Ethylene polymerization results for heterogeneous single and ternary catalyst systems based on hs MCM-41 at different reaction temperatures

Precursor(s) (ratio)	Temperature [°C]	Activity [kg PE/mol M h]	M_n [g/mol]	M_w [g/mol]	Modality[a]	wt% PE	wt% oligomer	PD
I	40	2255	110 485	343 890	m	100	0	3.113
I	60	2407	208 520	801 310	b	100	0	3.843
I	80	2310	46 630	132 550	m	100	0	2.843
II	40	1163	278 495	1 549 165	m	100	0	5.563
II	60	809	107 395	231 650	m	100	0	2.157
II	80	176	42 200	425 835	s	100	0	10.091
III	40	26 568	850	7520	m	21.1	78.9	8.870
III	60	26 537	1100	9690	s	23.3	76.7	8.796
III	80	12 238	1050	1670	m	37.0	63.0	1.588
I/II (1:1)	40	1470	145 280	415 440	m	100	0	2.860
I/II (1:1)	60	2130	94 780	267 330	m	100	0	2.821
I/II (1:1)	80	1636	55 390	194 070	m	100	0	3.504
I/II/III (4:4:1)	40	2841	5310	127 160	b	47.2	52.8	23.943
I/II/III (4:4:1)	60	3216	3860	104 910	s	62.9	37.1	27.173
I/II/III (4:4:1)	80	2240	7690	135 060	b	71.6	28.4	17.556

Polymerization conditions: method A; Al:M = 200:1; H_2O:Al = 0.9; *n*(metal):*m*(support) = 0.3 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

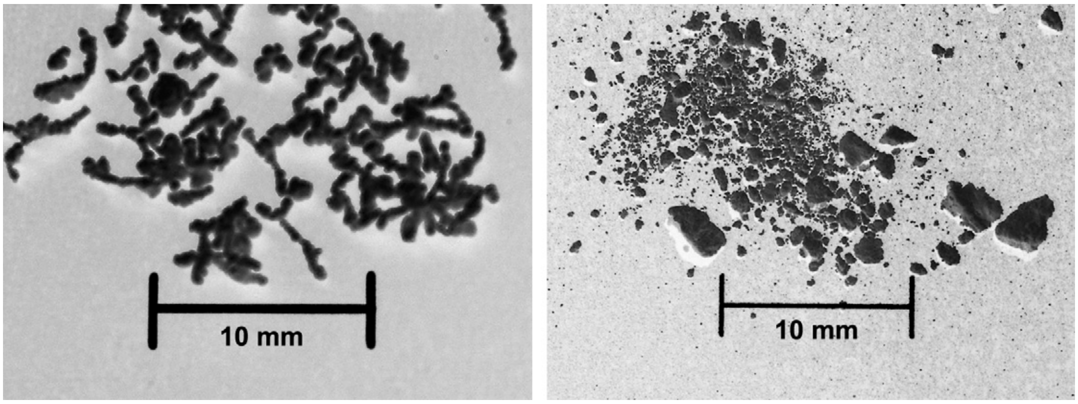
[a] s: shoulder; m: monomodal; b: bimodal.

ternary catalysts) while at higher temperatures a significant decrease in the activities could be noticed. The polyethylenes obtained with the single iron catalyst **III**/PHT showed very low molecular weights (M_ws). For the binary zirconium/titanium catalyst **I**/**II**/PHT, M_w decreases continuously at elevated temperatures while no dramatic temperature effect was observed for the ternary catalyst system. Analogous to the ‘‘fumed silica’’ based systems, high polydispersity values were obtained for polyethylenes produced with the ternary catalyst implicating bimodal molecular weight distributions. The product compositions obtained with the single iron catalyst **III**/PHT and the ternary catalyst **I**/**II**/**III**/PHT were analyzed. Interestingly, **III**/PHT produced more polymers at higher polymerization temperatures, but a levelling effect on the molecular weight (M_w) has to be noted resulting in a very low molecular weight polyethylene ($M_w = 1670$ g/mol) produced at 80 °C. The ternary hs MCM-41 based catalyst **I**/**II**/**III**/PHT showed the same behaviour as the corresponding ‘‘fumed silica’’ system. At elevated reaction temperatures, the contents of oligomeric products decrease dramatically. Again, an enhanced copolymerization rate of the titanium and zirconium centers can be assumed by removing the easily incorporated short-chain 1-olefins from the reaction solutions.

2.5. Morphologies and mean densities of the polymers

For industrial applications of the heterogeneous catalysts, not only the polymerization activities are the decisive factor. Besides the already mentioned polymer properties (M_w, MWD, melting point, melting enthalpy), the morphologies and mean densities of the obtained polyethylenes are very important. Selected polymer samples were therefore photographed with a digital camera (3× optical zoom, 6× digital zoom; pictures displayed as negatives), and their mean densities were determined. Polyethylene particles produced with homogeneous catalysts typically exhibit worm like structures (Scheme 16) with bends, branches, and rounded edges. Due to these sterically demanding particles, the mean densities are usually very low.

For comparison, photos were also taken from polyethylenes obtained with ‘‘fumed silica’’ based catalysts. Rigid particles



Scheme 16. Left: polyethylene produced with a homogeneous zirconocene dichloride/MAO catalyst. Right: polyethylene produced with **I**/PHT. Polymerization conditions: Al:M = 200:1; H_2O:Al = 0.9; ‘‘fumed silica’’ with *n*(metal):*m*(support) = 0.15 mmol/g; 250 ml *n*-pentane; 1 ml TIBA as 1 M solution in hexane; 60 °C; 1 h; 10 bar ethylene.

with more square-edged structures were observed for a polyethylene produced with **I**/PHT. These particles probably consist of very stable agglomerates with sizes between 0.55 mm and 3.30 mm. A high mean density of 378.4 g/l was determined for this polymer. Among the analyzed polymer samples, the polyethylene produced with a method A ternary catalyst (Zr:Ti:Fe = 8:8:1) exhibited the highest mean density (MD = 394 g/l).

3. Conclusion

Heterogeneous cocatalysts, catalysts, and catalyst mixtures for the polymerization of ethylene were prepared applying "fumed silica" and mesoporous MCM-41 support materials and zirconocene dichloride, titanocene dichloride, and a bis-(arylimino)pyridine iron complex as catalyst precursors. The catalyst mixtures produced polyethylenes which exhibit the properties of two single polymers. Interactions of the different active species became obvious due to different methods for the synthesis of the catalyst mixtures. The "fumed silica" and hs MCM-41 based catalysts exhibited higher polymerization activities than the corresponding homogeneous catalysts or heterogeneous catalysts based on common supports like "Davison silica". The investigation of different parameters (support material; H_2O:Al ratio; n(metal):m(support) ratio; method of catalyst synthesis; polymerization temperature; ratios of the applied metals) revealed that predictions of polymerization activities and polymer properties are somewhat difficult due to the complexity of the catalyst systems. Nevertheless, polyethylenes with the desired bimodal molecular weight distributions could be obtained with a series of ternary Zr/Ti/Fe catalysts. Both fractions of the bimodal polyethylenes consist of polymers with almost the same molecular weights as polyethylenes obtained with the single components. The ability of the zirconium and titanium species to copolymerize short-chain 1-olefins produced by the iron centers ("in situ" copolymerization) is therefore useful for the production of copolymers from only one monomer (ethylene).

4. Experimental

4.1. 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).

4.2. Gel permeation chromatography (GPC)

GPC measurements were routinely performed with a WATERS Alliance 2000 instrument at 150 °C containing a Mixed Bed PL lab column. As a solvent 1,2,4-trichlorobenzene was used.

4.3. Differential scanning calorimetry (DSC)

Melting points, melting enthalpies, and crystallinity values were determined with a NETZSCH DSC 2000 instrument. An amount of 3–5 mg of the polymer sample was applied by default. The melting point (156.62 °C) and the melting enthalpy ($\Delta H_m = 28.45$ J/g) of elemental indium served as calibration standards while the crystallinities were calculated as the ratio of the measured melting enthalpy and the melting enthalpy of 100% crystalline polyethylene ($\Delta H_{m,0} = 290$ J/g, extrapolated).

4.4. SEM and EDX measurements

SEM and EDX analyses of the heterogeneous catalysts and support materials were performed by SABIC Company (Riyadh, Saudi Arabia). The samples were placed on a sealed specimen holder (material: Al; diameter: 10 mm) and introduced into an Oxford ISIS300 instrument for EDX analyses (acceleration voltage: 20 kV; distance to the sample: 25 mm). After finishing the EDX analyses, the sealed sample was placed in a chamber and vaporized with gold and palladium (1 min; power: 20 mA). SEM measurements were then performed with a Cambridge S360 instrument (acceleration voltage: 20 kV; distance to the sample: 10–15 mm).

4.5. Photographs

Photographs of the polymer samples were taken with a CASIO QV-3000EX digital camera (3.3 megapixel; 3× optical zoom, 6× digital zoom). A black background was used. For better clarity, the photographs are displayed as negatives.

4.6. Mean density measurements

Mean densities were calculated using a 100 ml barrel and a balance. An amount of 100 ml of the polymer was filled in the barrel (without additional compaction by shaking) and weighed.

4.7. Synthesis of silica gel from sodium metasilicate

Sodium metasilicate (20 g) was neutralized with an excess of concentrated hydrochloric acid. The resulting highly viscous gel was filtered, washed with distilled water, dried on air, and finally calcined for 6 h at 540 °C.

4.8. Synthesis of heterogeneous catalysts with the PHT method

The finely powdered support material (0.5–3.0 g) was suspended in toluene (200 ml) and the desired amount of trimethylaluminum solution (2 M in toluene) was added. The suspension was heated to 40 °C and a defined amount of water was introduced as steam applying a wet argon stream. After cooling to room temperature, the catalyst precursor(s) were added as toluene (20 ml) solution(s), and the mixture was stirred at room temperature for 10 min. The resulting heterogeneous catalyst was filtered, washed with *n*-pentane (3×40 ml) and dried in vacuo (yields: ~96%).

4.9. Homogeneous polymerization of ethylene in the 1 l Büchi autoclave

An amount of 0.5–10 mg of the desired 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 1 l Büchi laboratory autoclave. The autoclave was thermostated to 60 °C and purged with ethylene (10 bar). After 1 h, the ethylene feed was stopped, the autoclave was cooled to room and the pressure was released. The resulting polyethylene was filtered and dried in vacuo.

4.10. Heterogeneous polymerization of ethylene in the 1 l Büchi autoclave

The finely powdered heterogeneous catalyst (0.02–1.5 g) was placed in a 1 l Büchi laboratory autoclave. *n*-Pentane (250 ml) and triisobutylaluminum (1 ml; 1 M in hexane) were added. The autoclave was thermostated at 60 °C applying an ethylene pressure of 10 bar. After 1 h, the ethylene feed was stopped, the autoclave was cooled to room temperature, and the pressure was released. The resulting polymer was filtered from the suspension and dried. If oligomers were present in the reaction mixtures, the suspensions were filtered, washed with *n*-pentane, diluted hydrochloric acid, water, acetone and, finally, *n*-pentane. The polymeric residue was dried in vacuo while the oligomer solutions were analyzed by gas chromatography.

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