Immobilization of η^5-cyclopentadienyltris(dimethylamido) zirconium polymerization catalysts on a chlorosilane- and HMDS-modified mesoporous silica surface: a new concept for supporting metallocene amides towards heterogeneous single-site-catalysts

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Abstract

The modification of a mesoporous silica surface with $Si(Ind)(CH_3)_2Cl$ and the immobilization of $CpZr(NMe_2)_3$ on this surface was studied via IR-spectroscopy. To reduce side reactions, the indenyl-modified silica was reacted with hexamethyl-disilazane (HMDS) under IR-control before the $CpZr(NMe_2)_3$-immobilization. The role of the hydroxyl group protection with HMDS is discussed. The surface modifications have been repeated via Schlenk technique at the same conditions and the surface modifications were studied with ^{13}C CP MAS–NMR, ^1H MAS–NMR, elemental-, SEM- and BET-analysis. The surface species of the resulting catalysts are discussed. The precatalysts have been treated with methylaluminoxane (MAO) (Al:Zr (mol:mol) = 500:1) and the resulting Zr contents (leaching-effect) are discussed. All catalysts have been tested in ethylene and propylene polymerization. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

To understand elementary steps in polymerization of olefins by Ziegler-type catalysts many investigations in homogeneous systems have been done [1–5], because these reactions are easier to understand in homogeneous than in heterogeneous systems [6].

The discovery that partially hydrolyzed alkyl aluminum compounds (MAO) increase the activity of metallocenes [7,8] as shown by Sinn and Kaminsky [9–17], and the introduction of *ansa*-zirconocenes by Brintzinger and Ewen [6,18,19] as homogeneous olefin polymerization catalysts activated with MAO,

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started a wide exploration of these systems [20–24]. For an industrial use in existing plants, metallocene catalysts have to be heterogenized due to the fact that current technology is based on gas phase and slurry processes [25]. On the other hand, the heterogenization of metallocene catalysts allows an improvement of polymer morphology, whereas reactor fouling and also the amount of MAO can be reduced [26–32].

As supports a wide range of materials like silica, alumina, zeolites, $MgCl_2$ [26,32–38] or organic carriers like cyclodextrins, polymers and starch [39–43] are used.

There are various immobilization techniques and strategies, the most common being impregnation techniques (simply removing the solvent from catalyst suspension in vacuo) or grafting techniques (washing and filtering the catalyst before drying). Either the metallocene is immobilized or the cocatalyst or both, in several steps or as reaction mixture. The analytical studies of such systems remain very complicated. If in case of silica, the support is treated with MAO at first, direct interactions between carrier and metallocene are excluded and the results in propylene polymerization are similar to those produced by homogeneous catalysts as found by Kaminsky and Renner [32]. The complexity of heterogenized systems after MAO-activation during the polymerization of olefins can be shown with electron paramagnetic resonance measurements. About 40% Zr^{III} could be detected in the Cp_2ZrCl_2/MAO system, during the ethylene polymerization [44]. Olivé and Olivé found approximately 70% Ti^{III} for the same homogeneous Ti system [45,46].

To prevent loss of activity, the fixed active catalytic centers and the vacant coordination sites have to be preserved for the olefins. But side reactions between the catalytic precursor and the surface lower the catalytic activity [47].

To examine the basic reactions during the immobilization, a better approach is to modify the surface with spacer-ligands at first and than, in a second step, to fix the metallocene precursor, with analytical analysis on every step as reported by Iiskola and coworkers [48–50].

There have been many affords to modify the surface (mainly of silica) with spacer ligands and generate the catalyst precursor on the surface [51–56]. The complexity of such systems prompted us to prepare a model system on silica, where simple surface modifying reactions and their analytical measurements can be done at every step, from the initial surface modification to polymerization.

We herein report the preparation of a chlorosilane compound as spacer ligand, of a zirconiumamide compound as Zr-precursor and of his anchoring on the modified mesoporous silica surface.

At first, the immobilization reactions were done on a pellet and examined via infrared spectroscopy. In the second part, silica samples have been prepared in toluene via Schlenk technique under the same conditions and examined with ^{13}C CP MAS–NMR, ^1H MAS–NMR, N_2-porosimetry (BET-measurements), elemental analysis and SEM-technique. The results of the spectroscopic examinations are discussed. Also polymerizations and reactions with MAO to examine the zirconium content after MAO-treatment, and polymerizations with these pretreated samples have been done.

2. Experimental

2.1. General procedures

All reactions were carried out under argon atmosphere using glove box and Schlenk techniques. THF and Et_2O were dried and deoxygenated by distillation over CaH_2 and sodium-benzophenone. Pentane and toluene were dried as described in [57]. Indene (Fluka, 80%) was distilled prior to use. Dicyclopentadiene (Merck Schucharth, dimer, >93%) was cracked and freshly distilled prior to use in synthesis. $ZrCl_4$ (Merck Schucharth, >98%), $LiNMe_2$ (Aldrich, 95%), dichlorodimethylsilane (Merck Schucharth, >98%), chlorotrimethylsilane (Merck Schucharth, >99%), hexamethyldisilazane (HMDS) (Merck Schucharth, >98%), Na_2SO_4 (Aldrich, 99.99%, activated at 120°C) and $NaNH_2$ (Merck Schucharth, >97%) were used without further purification.

Aeroperl 300/40 silica (Degussa, $300 \, m^2 \, g^{-1}$, pore volume $= 1.9 \, cm^3 \, g^{-1}$, particle size $= 40–120 \, \mu m$) was used as support. Methylaluminoxane (Witco, 30% in toluene) was used as cocatalyst. Ethylene (AGA Gas GmbH, grade 3.5) and propylene (Linde AG, grade 2.8) were purified by passing them through two purifi-

cation columns containing activated BTS-catalyst and molecular sieve (4 Å) before feeding the reactor.

2.2. Synthesis procedures

2.2.1. Synthesis of chlorodimethylinden-3-ylsilane

A solution of indene (10.04 ml, 109 mmol) in THF (20 ml) was added dropwise at room temperature under vigorous stirring to a suspension of $NaNH_2$ (4.68 g, 109 mmol) in THF (100 ml). The mixture was stirred overnight. The dark red solution was filtered, the solvent was removed in vacuo, and the remaining solid (NaInd) washed with hexane (2 × 25 ml). To a solution of dichlorodimethylsilane (7.9 ml, 65 mmol, 3 eq.) in 50 ml THF, a solution of NaInd (3 g, 22 mmol) in 25 ml THF was added dropwise at −30°C under vigorous stirring. The mixture was slowly warmed up to room temperature and stirred overnight. The brownish oily solution was separated, the solvent removed in vacuo and the solid washed with THF (3 × 20 ml). The brown oil, a mixture of chlorodimethylinden-3-ylsilane, di-indenyldimethylsilane, indene and higher oligomers, was distilled in vacuo. About 2 g (44%) of colorless chlorodimethylinden-3-ylsilane (boiling range: 80–95°C/0.2 mbar) could be isolated. ^{1}H NMR (CDCl$_3$): δ (ppm), 0.0 (3H, –CH$_3$); 0.05 (3H, –CH$_3$); 3.5 (1H, C$_3$–H); 6.5 (1H, C$_2$–H); 6.8 (1H, C$_1$–H); 7.0 (1H, C$_5$–H); 7.1 (1H, C$_6$–H); 7.3 (1H, C$_4$–H); 7.4 (1H, C$_7$–H). ^{13}C NMR (CDCl$_3$): δ (ppm), −0.1 (–CH$_3$); 0.0 (–CH$_3$); 47 (C$_3$); 121 (C$_4$); 123 (C$_7$); 124 (C$_6$); 125 (C$_5$); 131 (C$_1$); 133 (C$_2$); 142 (C$_{7a}$); 144 (C$_{3a}$). Anal. Calcd. for C$_{11}$H$_{13}$ClSi (%): C, 63.29; H, 6.28; Cl, 16.98; Si, 13.45. Found (%): C, 63.55; H, 6.30; Cl, 16.32.

2.2.2. Synthesis of tetrakis(dimethylamido)zirconium

About 6.99 g (30 mmol) of zirconium tetrachloride and 6.45 g (120 mmol) of lithiumdimethylamide were combined in the glove box. The reaction mixture was cooled to −196°C and 150 ml pentane were added slowly via cannula. The resulting suspension was slowly heated up to room temperature under vigorous stirring. After 4 days of stirring at room temperature, the solution was filtered off and the solid extracted with pentane (3 × 50 ml). The solvent was removed in vacuo

and the slightly yellow solid purified by sublimation (60°C/0.2 mbar). About 6.18 g (77%) of tetrakis(dimethylamido)zirconium were obtained. ^{1}H NMR (C$_6$D$_6$): δ (ppm), 3.0 (3H, –CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ (ppm), 39 (–CH$_3$). Anal. Calcd. for C$_8$H$_{24}$N$_4$Zr (%): C, 35.92; H, 9.04; N, 20.94; Zr, 34.10. Found (%): C, 35.32; H, 9.02; N, 20.78; Zr, 34.22.

2.2.3. Synthesis of η^5-cyclopentadienyltris(dimethylamido)zirconium

About 1.01 eq. of freshly distilled cyclopentadiene (0.75 g, 11.33 mmol) was added dropwise to a colorless solution of tetrakis(dimethylamido)zirconium (3 g, 11.22 mmol) in 30 ml toluene at −10°C. After refluxing the solution for 2 h, the solvent was removed in vacuo, to give the deep yellow liquid η^5-cyclopentadienyltris(dimethylamido)zirconium in quantitative yield. ^{1}H NMR (C$_6$D$_6$): δ (ppm), 2.9 (18H, –CH$_3$); 6.0 (5H, –C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): δ (ppm), 41.9 (–CH$_3$); 107.5 (–C$_5$H$_5$). Anal. Calcd. for C$_{11}$H$_{23}$N$_3$Zr (%): C, 45.79; H, 8.03; N, 14.56; Zr, 31.61. Found (%): C, 46.59; H, 7.82; N, 14.61; Zr, 31.54.

2.3. Synthesis of the precatalysts

2.3.1. Dehydratation of silica and preparation of the indenyl-modified support

Silica was first heated at 500°C in a nitrogen flow for 5 h and then kept under vacuum (2 × 10^{-4} mbar) during 12 h at the same temperature, in order to obtain the dehydroxylated silica.

Chlorodimethylinden-3-ylsilane (1.06 g, 5 mmol) was added dropwise at room temperature to a suspension of 4 g of dehydroxylated silica in 40 ml of toluene. The mixture was heated at 100°C for 8 h and then at 200°C for 4 h under refluxion. The liquid phase was separated by filtration and the solid washed with toluene (3 × 10 ml) and dried 30 h in vacuo at room temperature.

For the infrared experiments, the silane was introduced on the pellet via its vapor at 60°C. After reaction at 100 (8 h) and 200°C (4 h), the excess of chlorodimethylinden-3-ylsilane was condensed in a liquid nitrogen trap and removed. Finally, the pellet was treated under dynamic vacuum at 100°C during 2 h in order to remove all volatile compounds.

2.3.2. Reaction of HMDS with the indenyl-modified support

HMDS (0.32 g, 2 mmol) was added dropwise to a suspension of 1.5 g of the indenyl-modified support in 20 ml of toluene under stirring at room temperature. After stirring for 13.5 h at room temperature, 1 h at 60°C and 0.5 h at 70°C, the solid was filtered off, washed with toluene (3 × 10 ml) and dried 30 h in vacuo at room temperature. For the infrared experiments, HMDS was introduced as vapor at room temperature while the heating procedure was the same as above. The excess of HMDS was removed by use of a liquid nitrogen trap and the pellet was treated at 70°C in a dynamic vacuum for 20 h.

2.3.3. Preparation of precatalyst A

About 2 g of the indenyl-modified support were suspended in 20 ml of toluene. After addition of 0.73 g (2.5 mmol) of η^5-cyclopentadienyltris(dimethylamido)zirconium, the suspension was heated to 120°C under stirring for 3 h. The resulting solid, called precatalyst A, was filtered, washed with toluene (3 × 10 ml) and dried at room temperature for 30 h in vacuo.

2.3.4. Preparation of precatalyst B

About 1.5 g of the indenyl- and HMDS-modified support were suspended in 20 ml of toluene. After addition of 0.55 g (1.9 mmol) of η^5-cyclopentadienyltris-(dimethylamido)zirconium, the suspension was heated to 120°C for 3 h under stirring. The resulting solid, called precatalyst B, was filtered, washed with toluene (3 × 10 ml) and dried in vacuo at room temperature for 30 h.

2.4. Physicochemical characterization of the precatalysts

All solids were characterized by various methods. The infrared spectra were recorded on a Nicolet Magma IR 550 and a Perkin-Elmer FT-IR 1600. For studies of the reactions of the indenyl-modified silane and HMDS an infrared cell with CaF$_2$-windows analogous to [58] and allowing in situ studies was used.

MAS–NMR experiments were recorded on a Bruker DSX-300 spectrometer equipped with a multi-nuclear magic-angle spinning probe-head. The ^{13}C CP MAS–NMR spectra were obtained at 75.47 MHz with a 5 ms contact time and a 1 s delay between the scans (ca. 5000 transients were accumulated). ^{1}H MAS–NMR spectra were obtained at 300.18 MHz (32 transients, recycle delay 1 s). In all cases, the spinning rate was 8 kHz.

Elemental analysis for carbon, hydrogen and nitrogen were determined on a Vario EL analyzer. The zirconium contents were determined on a Schimadzu UV-160 photometer and the aluminum contents on a Varian Spectr-AA 400 spectrometer.

The nitrogen adsorption/desorption isotherms were carried out on a Micromeritics ASAP 2000 equipment. The scanning electron micrographs were obtained on a Jeol, JSM-5900 LV Scanning Electron Microscope at 5 and 15 kV.

2.5. Polymerization and polymer-analytical procedures

2.5.1. Polymerization procedure

In a glove box 10 mg (200 mg) of the precatalyst were dissolved/suspended in 50 ml (30 ml) of toluene in a Schlenk tube. The appropriate amount of MAO (30% in toluene, Al/Zr = 500) was then added slowly under stirring upon a color change from yellow to orange occurred. The reaction mixture was stirred overnight at room temperature.

A 0.5 l Buechi glass-autoclave, equipped with a pressflow gas controller was filled with approximately 230 ml of dry and oxygen-free toluene. The autoclave was pressurized with ethene or propene and thermostated to the reaction temperature. The desired amount of catalyst/MAO solution/suspension was transferred into the injection system via syringe or cannula, the injection system closed, the solution/suspension injected into the autoclave and the injection system washed with an additional 5 ml of toluene. The pressure was kept constant during the polymerization and the amount of ethene consumed by the catalyst during the reaction was measured. The polymerization was quenched after 1 h by adding 10 ml of acidic methanol and the resulting polymer-suspension was poured into 250 ml of methanol–HCl mixture (3:1) and stirred for 16 h to precipitate the polymer. After filtration, the polymer was dried at 60°C in vacuo. If no

polymer/oligomer precipitated, the solution was treated with dilute HCl, water and methanol. The organic layer was separated and the solvent removed in vacuo. The molecular weight determination of the polymers was performed on a combination of a Waters 150 CV–high-temperature GPC at 135°C with 1,2,4-trichlorobenzene as solvent and a modified Whyatt Mini Dawn light-scattering instrument. The calibration was performed with polystyrene standards and conversion into PE- and PP-calibration curves using Mark-Houwink parameters. Melting points determinations (T_m) were carried out on a Netzsch TASC 414/2 differential scanning calorimeter (DSC) upon reheating the polymer sample to 220°C at a heating rate of 3°C min^{-1}.

2.5.2. Leaching of the catalysts

The precatalysts, suspended in 5 ml toluene, were reacted with a MAO/toluene solution (30%, ratio Zr:Al (mol:mol) = 1:500) at room temperature under stirring in the glove box for 24 h. After the reaction, the solids were separated by centrifugation, washed with toluene (3 × 5 ml) and dried for 30 h in vacuo at room temperature.

3. Results and discussion

3.1. Modification of the silica surface

3.1.1. Reaction with Si(Ind)(CH$_3$)$_2$Cl

The infrared spectrum of silica, dehydroxylated under vacuum at 500°C, shows in the ν(O–H) range a strong band at 3750 cm^{-1} together with a small broad shoulder near 3650 cm^{-1} (Fig. 1a), attributed to isolated and H-bonded hydroxyl groups, respectively. When chlorodimethylinden-3-ylsilane is adsorbed on silica at room temperature, the infrared spectrum is greatly modified, the ν(O–H) band at 3750 cm^{-1} being shifted to ca. 3600 cm^{-1} and new bands appearing in the ν(C–H) range (Fig. 1b). No gas evolution is observed in agreement with literature data, which indicate that at room temperature just physical adsorption of the chlorosilanes takes place, and that it is necessary to increase the reaction temperature to 150°C in order to observe a reaction with the support [59]. After heating to 200°C, HCl is observed in the gas phase showing that the well known reaction between chlorosilanes and silica [59–66] has occurred (Scheme 1).
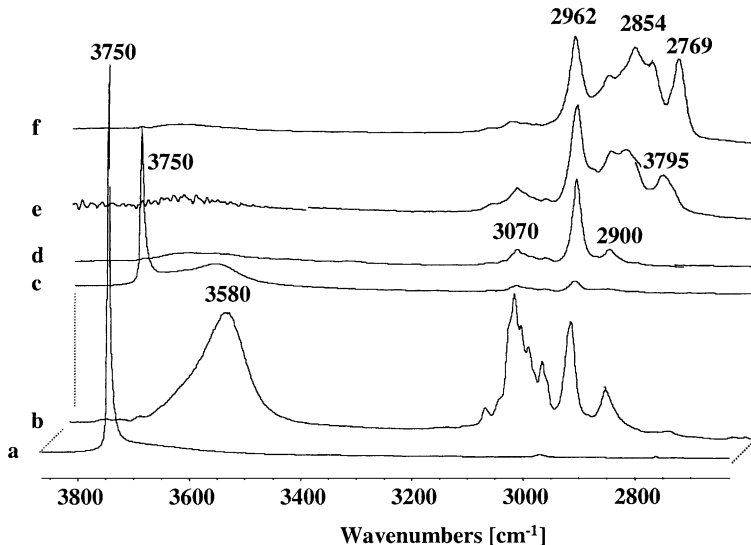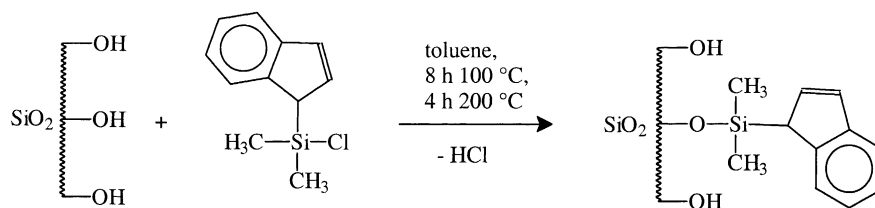

Fig. 1. Infrared spectra (in the 4000–2700 cm^{-1} range) of: (a) silica dehydroxylated at 500°C; (b) physisorption of Si(Ind)(CH$_3$)$_2$Cl on (a) at room temperature; (c) after grafting of Si(Ind)(CH$_3$)$_2$Cl on (a) at 200°C and removal of the excess of chlorosilane; (d) sample (c) after reaction with HMDS; (e) sample (c) after reaction with ZrCp(NMe$_2$)$_3$; (f) sample (d) after reaction with ZrCp(NMe$_2$)$_3$.

Scheme 1. Modification of the silica surface at 100 and 200°C with chlorodimethylinden-3-ylsilane.

After removal of the excess of chlorosilane and of the hydrochloric acid, the infrared spectra shows the following features (Fig. 1c): (i) a non-negligible amount of silanol groups at $3750\,cm^{-1}$ have been restored, showing that the grafting reaction is not complete; (ii) a new ν(O–H) band appears at $3630\,cm^{-1}$, attributed to silanol groups in interaction with the chemisorbed chlorosilane; (iii) ν(C–H) bands, characteristic of the indenyl and methyl moieties, appear near $3000\,cm^{-1}$. All these features are in agreement with the reaction depicted in Scheme 1.

The solid-state NMR examinations are also in agreement with these conclusions (Figs. 2 and 3). After reaction of the dehydroxylated support with the indenylsilane at 200°C one signal at ca. 2 ppm (attributed to the protons of isolated silanol groups, Fig. 2a) can be observed. In addition to this signal, three other signals at ca. 0, 4 and 7 ppm, attributed to the Si–CH$_3$, C$_3$–H of the indenyl group and aromatic and olefinic protons of the indenyl moiety are detected. Similarly, the ^{13}C CP MAS–NMR spectrum shows the presence of the Si(Ind)(CH$_3$)$_2$ fragment on the surface (Fig. 3a): signals at 0 (Si–CH$_3$), 47 (aliphatic carbon atom of the five-membered ring of the indenyl spacer), 125 (aromatic carbons of indenyl), 129 and 130 (olefinic carbon atoms) and 144 ppm (quaternary carbons).

During the reaction of chlorosilanes with silica, no side reactions resulting in the reopening of siloxane bridges, as reported by Borello et al. with alcohols [67] or from the reaction of silica with the reaction product HCl, as reported from Hertl during the reaction of silica with methanol [68] could be observed [69,70]. During the reaction of chlorosilanes with silica, an initial fast reaction of about 10–15% of direct replacement of hydroxyl groups by a Cl group has been observed from Hair and Hertel [71]. Our examination concerning the chlorine amount before and

after the reaction shows that less than 1% of the used chlorodimethylinden-3-ylsilane reacts according to this pathway, if all detected chlorine originates from this side reaction. Nevertheless, about 0.9 indenyl spacers per nm^2 (4.76 wt.% carbon) can be fixed on the surface at this conditions.

3.1.2. Reaction of the modified silica with HMDS

As mentioned above, a non-negligible amount of silanol groups did not react with the chlorosilane. These silanol groups can be responsible for side-reactions during the grafting of zirconium. As a consequence, it is necessary to remove them. The reaction of the chlorosilane compound can be one way with silica at higher temperatures. This had been achieved at 300–400°C with methylchlorosilanes [62] but Si(Ind)(CH$_3$)$_2$Cl is not stable at these reaction conditions for a longer period of time.

Another way, commonly used in catalysis, chromatography and tailoring of silica surfaces [64,72–77], is the silylation of isolated silanol groups with HMDS, leading to the formation of hydrophobic Si(CH$_3$)$_3$ groups on the silica surface. The synthesis and properties of HMDS towards chemical reactions are well known and were already described by Sauer and coworkers in the 40s [78,79]. Hertl and Hair determined that the reaction of free silanols of chemically unmodified silica and HMDS followed a second-order kinetic law with an activation energy of $18.5\,kcal\,mol^{-1}$ [76]. Only a small fraction of H-bonded hydroxyl groups react with HMDS [76]. Further, advantages of HMDS towards reaction with silica is the high reaction rate already at 30°C [76].

Infrared spectroscopy shows that after reaction with HMDS (Scheme 2) at 70°C nearly all isolated silanol groups (characterized by the ν(O–H) band at $3750\,cm^{-1}$) have disappeared (Fig. 1d). In addition, the increase of the C–H streching bands at 2962
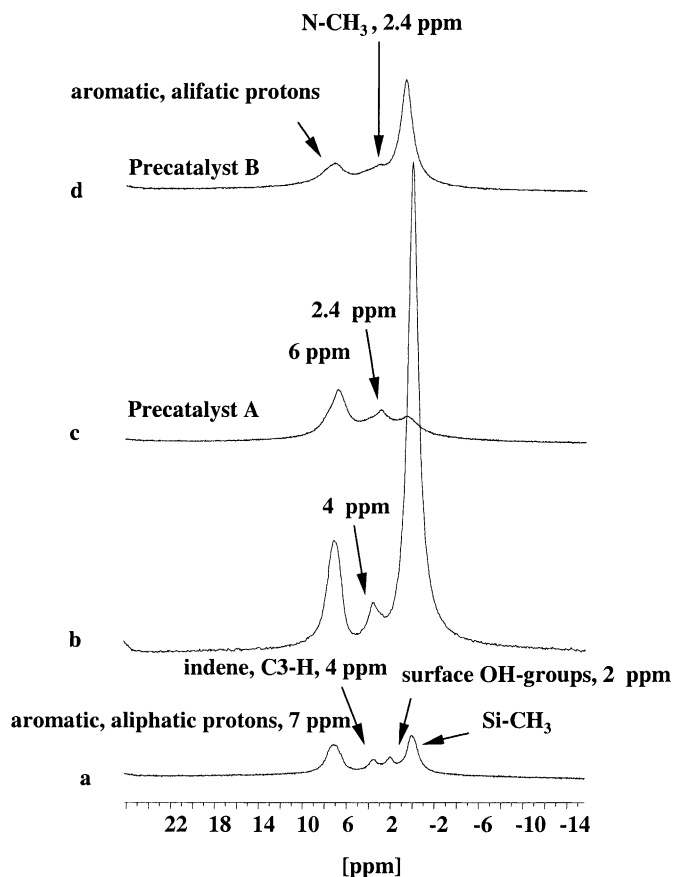
N-CH$_3$, 2.4 ppm

aromatic, alifatic protons

Precatalyst B

d

2.4 ppm

6 ppm

Precatalyst A

c

4 ppm

b

indene, C3-H, 4 ppm   surface OH-groups, 2 ppm

aromatic, aliphatic protons, 7 ppm   Si-CH$_3$

a

22 18 14 10 6   2   -2 -6 -10 -14

[ppm]

Fig. 2. ^{1}H MAS–NMR of: (a) silica dehydroxylated at 500°C after reaction with Si(Ind)(CH$_3$)$_2$Cl at 200°C and removal of the physisorbed species; (b) solid (a) after reaction with HMDS; (c) precatalyst A (reaction of zirconium complex with (a)); (d) precatalyst B (reaction of zirconium complex with (c)).

and 2904 cm^{-1} clearly displays the progress of the reaction via Scheme 2.

The solid-state NMR results are also in agreement with these results: both the ^{1}H and ^{13}C NMR spectra (Figs. 2b and 3b) show the increase of the signal intensity of methyl groups bound to silicon, while microanalysis gives a carbon content of ca. 5.32 wt.%.

3.1.3. Immobilization of η^5-cyclopentadienyltris-(dimethyl)amidozirconium on the indenyl-modified silica surface

Zirconium amide complexes are well known and suitable compounds for the preparation of metal-locenes [50,80–84]. The basicity of dimethylamine is high, allowing molecules with acidic protons like 1,3-cyclopentadiene or indene to be deprotonated with HNMe$_2$ formation. The use of amido instead of chlorozirconium precursors avoids the necessity of metallating the fixed ligand on the surface [48,49,85,86]. Also salt formation and the difficult removal from the surface can be avoided by this way [87]. In addition, the reaction product dimethylamine produced via Scheme 3 is gaseous at room temperature and can be easily removed in vacuo from the surface.

When η^5-cyclopentadienyltris(dimethyl)amidozirconium is adsorbed on the indenyl-modified silica at room temperature, the band at 3750 cm^{-1}, characteristic of isolated silanol groups, totally disappears. Only a small broad band at 3680 cm^{-1}, resulting
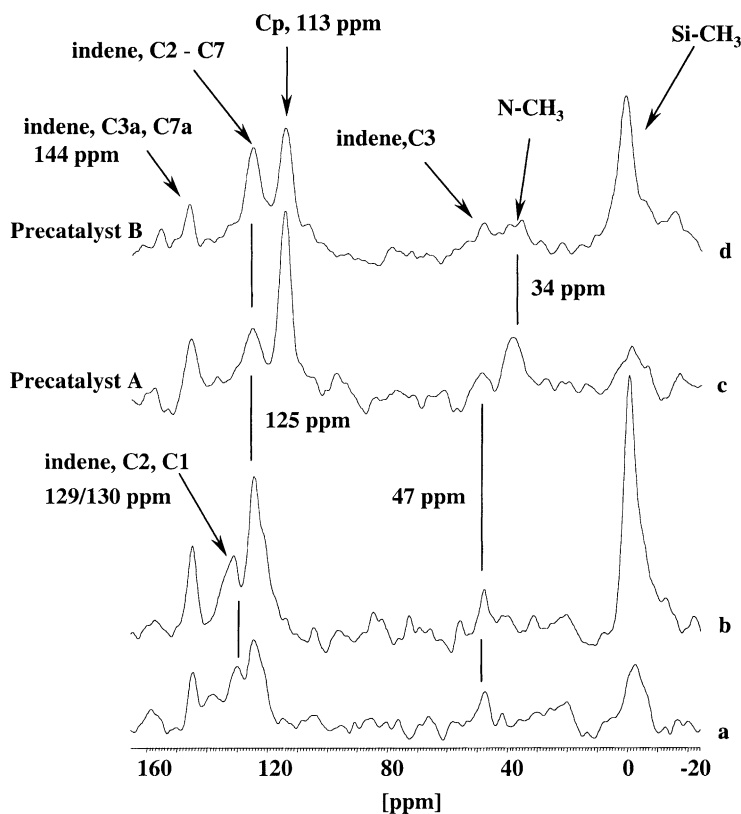
Fig. 3. ^{13}C CP MAS–NMR of: (a) silica dehydroxylated at 500°C after reaction with Si(Ind)(CH$_3$)$_2$Cl at 200°C and removal of the physisorbed species; (b) solid (a) after reaction with HMDS; (c) catalyst A (reaction of zirconium complex with (a)); (d) catalyst B (reaction of zirconium complex with (b)).

from inner and sterically hindered silanols remains (Fig. 1e). Dimethylamine, formed during the reaction of ZrCp(NMe$_2$)$_3$ with the silanol groups is detected by a small infrared band at 3270 cm^{-1}, arising from its physisorption on the silica pellet. Infrared spectroscopy cannot indicate if, in addition to the reaction with the remaining hydroxyl groups, the expected reaction with the indenyl fragment occurred. However, such informations can only be obtained from solid-state NMR. As ^{1}H MAS–NMR shows the appearance of the signal of the methyl group of the amido group at 2.4 ppm (Fig. 2c), it is difficult to determine, from this spectrum, if the indenyl group has lost one proton. ^{13}C CP MAS–NMR is more informative: the aliphatic carbon (at 47 ppm) and the olefinic carbon (at 130 ppm) signals have completely disappeared, while the quartenary carbons are shifted

10 ppm to lower field and the aromatic indenyl carbons nearly 10 ppm to higher field, showing that the indenyl spacer has been deprotonated. In addition to these peaks, the cyclopentadienyl moiety of the zirconium complex gives a signal at 113 ppm and the methyl group of the amido ligand gives a signal at 34 ppm.

The zirconium content of the solid (4.7 wt.%, corresponding to 1.5 Zr nm^{-2}) is in agreement with a reaction with both the hydroxyl groups and the indenyl spacer (whose loading was 0.9 nm^{-2}). The nitrogen content of the sample is 0.43 ± 0.2 wt.% corresponding to a N/Zr ratio of 0.3–1. This value clearly indicates that, in the solid, the zirconium complex has retained zero or one amido group. The loss of the three amido groups of the ZrCp(NMe$_2$)$_3$ complex should be accompanied by the creation of three bonds with
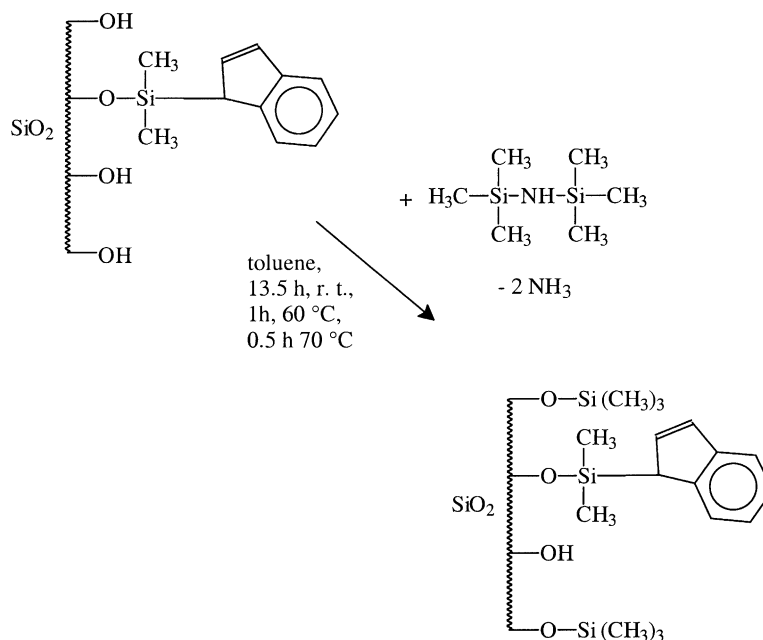
Scheme 2. Silylation of the indenyl-modified silica surface with HMDS.

the surface. Due to the high dehydroxylation temperature and the fact that almost all hydroxyl groups are isolated, the most probable structure for this triply surface-bonded species is the one depicted as species IV in Scheme 3. A complex doubly bonded to the surface could be either species II (reaction with one hydroxyl group and one indenyl spacer) or species III (reaction with two hydroxyl groups). A structure like species I or V where zirconium is bound to the surface via only one bond is improbable, due to the low nitrogen loading. This solid, which contains at least three different zirconium species, will be denoted as precatalyst A in the following.

3.1.4. Immobilization of η^5-cyclopentadienyltris-(dimethyl)amidozirconium on the indenyl- and HMDS-modified silica surface

As mentioned above, ZrCp(NMe$_2$)$_3$ can react with both the indenyl spacer and the remaining hydroxyl groups on the silica surface. We then decided to study its reactivity with the modified silica where most of the remaining hydroxyl had been removed by reaction with HMDS. The resulting infrared spectrum is shown on Fig. 1f. No conclusion can be drawn from this spectrum. On the other hand, chemical analysis gives some interesting features: (i) the zirconium loading is now 3.11 wt.% (corresponding to 1.1 Zr nm^{-2}) a value which is 30% lower than that achieved on the support without treatment with HMDS; (ii) the N/Zr molar ratio of the solid is now 1.3 ± 0.3, showing that there is one or two amido groups in the coordination sphere of zirconium and that, in this case, the structure IV is less probable. ^{1}H MAS–NMR and ^{13}C CP MAS–NMR experiments show that most of the indenyl fragments have been deprotonated, allowing to reasonably conclude that a structure like V is of minor importance. In the solid, the resulting zirconium-species should have the structures I or II (note that the zirconium content, 1.1 nm^{-2}, is quite the same than the indenyl spacer, 0.9 nm^{-2}). This solid is called precatalyst B in the following.

3.1.5. Morphology of precatalysts A and B

The SEM-pictures of the support and of the precatalysts (Fig. 4) show a fragmentation of the support during the modification reactions. Additional examinations showed that this fragmentation originated from the stirring of the samples during the reactions and
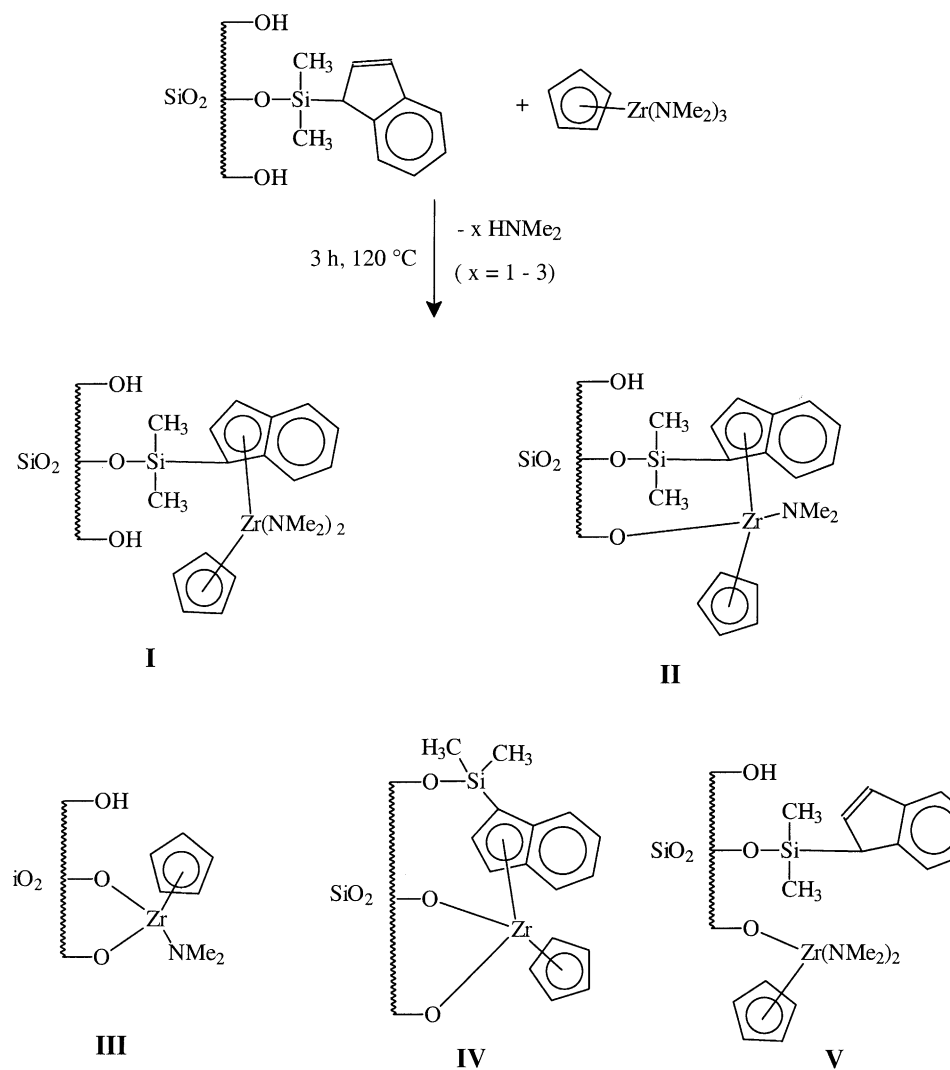
Scheme 3. Reaction of η^5-cyclopentadienyltris(dimethylamido)zirconium with the indenyl-modified silica surface and proposed Zr-species.

especially during the drying of the catalysts in vacuo. The mean diameter of the particles varies between 40 and 120 μm. However, this macroscopic modification of the material has only a slight influence on the adsorption characteristics of the carriers (Table 1).

These data show that the three supports are related to mesoporous morphology-materials with a surface area around $200\,\mathrm{m^2\,g^{-1}}$. The slight decrease of the surface area and of the pore volume after the grafting reactions is probably related to: (i) the fact that in 1 g of precatalyst there is less than 1 g of support,

due to the presence of spacer, zirconium complex and HMDS; (ii) the spacer and the zirconium complex are grafted in the mesopores, resulting in a decrease of the accessible volume of the pores.

3.2. Polymerization studies

3.2.1. Polymerization of ethylene

The ethylene polymerization results with precatalysts A, B and the precursor $CpZr(NMe_2)_3$ are listed in Table 2.
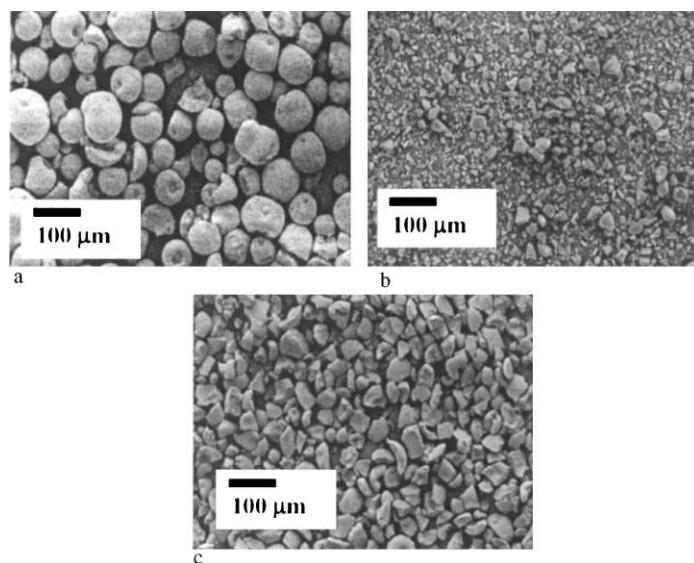
Fig. 4. SEM pictures of: (a) initial support; (b) precatalyst A; (c) precatalyst B.

Table 1
BET-surface and pore characteristics of the support and precatalyst A and B

	Support	Precatalyst A	Precatalyst B
Surface area[a] ($m^2 g^{-1}$)	255	211	183
Cumulative pore volume of pores[b] ($cm^3 g^{-1}$)	1.64	1.29	1.07
Average pore diameter of pores[b] (Å)	254	215	198

[a] BET.
[b] BJH, desorption, 17–1000 Å diameter.

Fig. 5 shows the activity of the three catalysts as a function of time. It can be seen that $CpZr(NMe_2)_3$ which is the most active catalyst, is rapidly deactivated. One reason could be the observed reactor fouling. The two supported catalysts are less rapidly deactivated, probably due to a slighter reactor fouling, the conversion being smaller. The comparison of the initial activities shows that the homogeneous catalyst is the more active one, due to the fact that the two supported catalysts can contain various zirconium-species

Table 2
Polymerization results with precatalyst A, B and $CpZr(NMe_2)_3$[a]

	Precatalyst A	Precatalyst B	$CpZr(NMe_2)_3$
Zr (wt.%)	4.70	3.11	31.61
Maximum activity (kg PE mol^{-1} Zr bar^{-1} h^{-1})	1.50×10^3	1.60×10^3	4.50×10^3
Average activity (kg PE mol^{-1} Zr bar^{-1} h^{-1})	1.36×10^3	0.70×10^3	1.65×10^3
$M_w \times 10^5$ ($g\, mol^{-1}$)	3.88	3.46	4.60
$M_n \times 10^5$ ($g\, mol^{-1}$)	0.93	0.83	2.10
D	3.35	4.17	2.19
m_p (°C)	134.20	134.10	134.20

[a] Cocatalyst MAO (Al/Zr (mol/mol) = 1000), polymerization temperature 40°C, 2 bar, polymerization time 1 h.
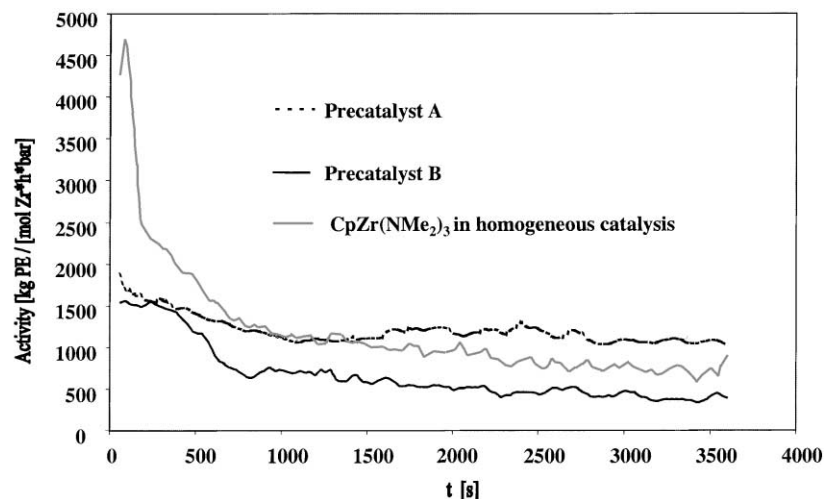
Fig. 5. Polymerization behavior of the MAO activated precatalyst A, B and η^5-cyclopentadienyltris(dimethylamido)zirconium (Al/Zr (mol/mol) = 1000, 40°C, 2 bar, 1 h).

which are more or less active. The higher polydispersities of the polymers obtained with the heterogeneous catalyst compared to the polymers obtained with the homogeneous one are in agreement with that results.

The higher polydispersities of the polymers obtained with catalyst B indicate that, in consequence of the HMDS-treatment before the immobilization of CpZr(NMe₂)₃, more polymerization active Zr-species are generated on the silica surface.

The higher degree of deactivation of catalyst B (which contains monografted complexes) compared to catalyst A (which contains more bigrafted species) can be related to a leaching-effect, which should be more easier for monografted complexes than for bigrafted ones. For this reason, we decided to study the leaching process on the two catalysts.

3.2.2. Leaching experiments with MAO

For this purpose, the catalysts were first treated with a MAO/toluene solution (30%, Al/Zr (mol/mol) = 500); the resulting catalysts were then characterized and used in ethylene polymerization. The results of the analysis of the solids are given on Table 3.

The very high amount of aluminum on the solids, due to the adsorption of MAO on the silica support can explain the decrease of the zirconium loadings on the two catalysts, even if it cannot be excluded that some leaching occurred during this step. The catalytic

results obtained with these "preactivated" catalysts are more interesting (Fig. 6 and Table 4). Indeed, a deactivation can be observed due to reactor fouling, as in the case of the homogeneous catalyst. This can be explained by the formation of ionic zirconium-species during the treatment with the MAO, which are the active sites for the polymerization and which are rapidly removed from the solid. Table 4 shows that the preactivated catalysts are less active than the non-preactivated ones, probably due to a loss of zirconium during the activation, even if it is not shown by the chemical analysis. It has to be pointed out that the decrease of the activity of precatalyst A upon treatment of MAO is more significant than that of precatalyst B, showing that the Si–O–Zr bridges are more easily broken

Table 3
BET and metal analysis after MAO-treatment

	Catalyst A	Catalyst B
Al (wt.%)	31.80	30.40
Zr (wt.%)	1.03	0.87
Surface area[a] (m² g⁻¹)	249	244
Cumulative pore volume of pores[b] (cm³ g⁻¹)	0.21	0.18
Average pore diameter of pores[b] (Å)	70	83

[a] BET.
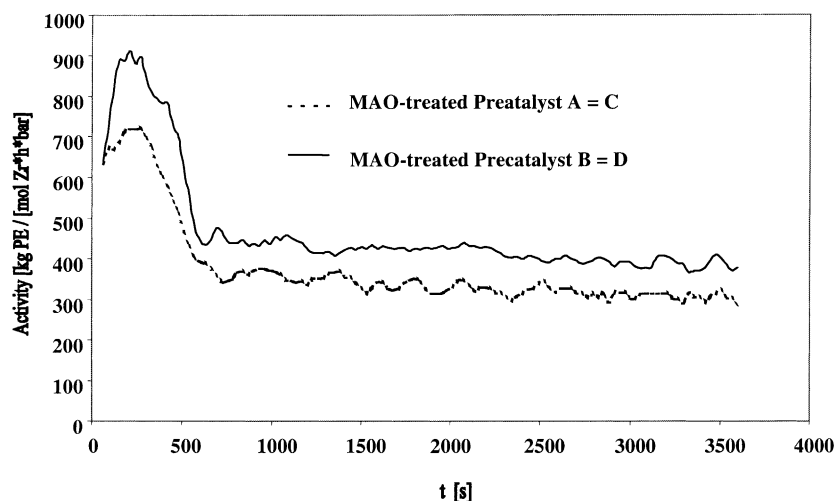[b] BJH, desorption, 17–1000 Å diameter.

Fig. 6. Evolution of the activity as a function of time for the preactivated catalysts.

Table 4
Polymerization results and polymer weights with the MAO-treated precatalyst A (= C) and B (= D)[a]

	MAO-modified precatalyst A = C	MAO-modified precatalyst B = D
Maximum activity (kg PE mol^{-1} Zr bar^{-1} h^{-1})	0.90×10^3	0.70×10^3
Average activity (kg PE mol^{-1} Zr bar^{-1} h^{-1})	0.38×10^3	0.47×10^3
$M_w \times 10^5$	4.36	6.04
$M_n \times 10^5$	1.47	1.71
D	2.96	3.53
m_p (°C)	135.00	139.20

[a] Cocatalyst MAO (Al/Zr (mol/mol) = 1000), polymerization temperature 40°C, 2 bar, polymerization time 1 h.

than the bonds between the indenyl fragment and zirconium.

The molecular weights of the polymers obtained after preactivation of the catalysts are higher than those obtained by ordinary activation. A decrease of the polydispersities can also be observed.

The polydispersities of the polymers obtained with catalyst D (equal to precatalyst B) are higher in comparison to the polymers obtained with catalyst C (equal to precatalyst A). We assume that the polymerization active Zr-species in the case of catalyst D are mainly of the types I and II (Scheme 3). In the case of catalyst C, the polymerization active Zr-species mainly consists of species III.

The two catalysts were also used in propene polymerization, but they gave only poor polymerization activity of 100–500 kg PP mol^{-1} Zr bar^{-1} h^{-1}. The produced polypropene were atactic and of low molecular mass, resulting in oily liquids. No activity was observed with the preactivated catalysts.

4. Conclusion

A dimethylinden-3-ylsilane spacer has been anchored on a thermally treated mesoporous silica-surface. The low reactivity of chlorosilanes with silica surfaces was shown by IR-spectroscopy. $CpZr(NMe_2)_3$ was immobilized on this surface under dimethylamine elimination. This unselective pathway generates several Zr-surface species. In a better approach towards heterogeneous single-site-catalysts, the unreacted hydroxyl groups have been silylated after anchoring the indenyl-spacer with HMDS. HMDS

is a very versatile reagent to minimize side reactions in the third step of the $CpZr(NMe_2)_3$-immobilization. Without OH-silylation more Zr-surface species were generated, but less polymerization active centers could be generated by MAO activation compared to the HMDS-silylated catalyst.

The first surface reaction in $CpZr(NMe_2)_3$-immobilization is the reaction of the precursor with sterically hindered surface hydroxyl groups, in a second step the desired deprotonation of the anchored indenyl-ligand takes place. The content of the desired species increased after HMDS-treatment of the indenyl-modified support.

In ethene polymerization, the non HMDS-treated catalyst shows higher activity, produces higher molecular weight polymers with lower polydispersities. They only differ in the concentration of the polymerization active species resulting in the lower activities of the heterogeneous catalyst.

In propene polymerization, the catalysts only show low activity of about $100–500 \, kg \, PP \, mol^{-1} \, Zr \, bar^{-1} \, h^{-1}$ and only produce atactic polymer.

A MAO-treatment of the precatalysts (Al/Zr (mol/mol) = 500) results in a dramatic decrease of pore volume, Zr content and polymerization activity. The BET surface of the precatalysts and the molecular weights of the produced polymers have been increased significantly in ethene polymerization (Al_{total}/Zr (mol/mol) = 1000), also the melting points of the polymers. After the MAO-treatment, the polymer dispersities have decreased. The HMDS-treated catalysts now produce higher molecular weights and polymer dispersity in comparison to the non HMDS-treated catalyst. The polymerization activity is increased with the HMDS-treated catalyst compared to the unmodified one. The MAO-treated catalysts are completely unactive in propene polymerization. Nevertheless, we could show that an approach towards heterogeneous single-site-catalysts by the used step-by-step one-pot synthesis of the precatalyst is possible.

Acknowledgements

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