

Heterogenization of racemic ethylenebis(1-indenyl)zirconium dichloride on trimethylaluminum vapor modified silica surface

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Abstract

Heterogeneous metallocene catalysts were prepared by adsorbing *rac*-Et(Ind)₂ZrCl₂ on a modified silica surface in solution. The modification of silica was conducted in gas phase with atomic layer chemical vapor deposition (ALCVD) technique, where the silica, preheated at either 350 or 600°C, was allowed to react with vaporized trimethylaluminum (TMA) at 250°C. Modified carriers and heterogeneous catalysts were characterized with FTIR, ¹H MAS (magic-angle spinning) NMR, ¹³C, and ²⁹Si CP (cross-polarization) MAS NMR spectroscopies and elemental analyses. In the reaction of TMA with silica, a saturated surface was formed consisting of different (–O)_{4–n}Si(CH₃)_n (*n* = 1, 2 or 3) and –AlCH₃ groups. The ratio of –SiMe to –AlMe groups was approximately 1.5 in the TMA/SiO₂ carriers. When the metallocene was adsorbed onto the carrier it seemed to react with the surface –AlCH₃ groups and possibly –ZrCH₃ groups were formed. Heterogeneous catalysts were tested in the polymerization of ethylene and propylene in the presence of methylalumoxane (MAO). And they produced similar polymer as the homogeneous *rac*-Et(Ind)₂ZrCl₂ catalyst, but with lower activity. A catalyst with the best activity was achieved from silica that was preheated at 600°C. Moreover, leaching of catalyst was examined whereupon a part of zirconium was observed to desorb from the carrier. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Several studies during the 1990s have been devoted to heterogenize metallocene catalysts

on support material because industrial applications are usually based on heterogeneous catalysts [1,2]. The use of heterogeneous catalysts prevents reactor fouling and enables the control of size and shape of polymer particles [3]. In addition, lower amount of methylalumoxane (MAO) is needed to activate the heterogeneous catalysts or alternatively MAO can be replaced with cheaper cocatalysts [2].

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Various immobilization methods have been reported [2], where the support material can be either inorganic (e.g. SiO_2) or organic (e.g. polystyrene). One way to prepare a heterogeneous catalyst is to adsorb the metallocene complex directly onto the carrier surface, but usually the carrier is pretreated with, for example, MAO or aluminum alkyls before adsorption of the metallocene. The third method is to first attach the cyclopentadienyl ligands to the support and then introduce the metal compound, for example, ZrCl_4 , onto the carrier. Furthermore, heterogeneous catalysts can be prepared so that the metallocene itself is both the catalyst and the monomer [4]. The polymerization properties of the heterogeneous catalysts depend on the used heterogenization method [1,2].

In our study, atomic layer chemical vapor deposition (ALCVD) technique was used to modify silica with trimethylaluminum (TMA). In this procedure, TMA is first vaporized and then with a help of nitrogen gas it is brought into a contact with the silica. In the open literature, this method, also called as atomic layer epitaxy (ALE) technique, is rarely applied in the preparation of polymerization catalysts, but there are some references where this technique has been used to modify the silica surface [5,6]. In the patent literature, this technique has been used to vaporize, e.g. ZrCl_4 [7] and Cp_2ZrCl_2 [8] onto the silica. ALCVD technique is a surface-controlled way to introduce adsorbent on the carrier, because bonding is based on chemisorption and only one molecular layer or fraction thereof is formed at a time on the surface [9]. After TMA treatment, the synthesis of the heterogeneous catalysts was continued in solution where the metallocene, $\text{rac-Et(Ind)}_2\text{ZrCl}_2$, was adsorbed on the carrier. Modified carriers and heterogeneous catalysts were characterized with FTIR, ^1H MAS (magic-angle spinning) NMR, ^{13}C , and ^{29}Si CP (cross-polarization) MAS NMR spectroscopy. The catalysts were tested in the polymerization of ethylene and propylene in the presence of MAO. Leaching of the catalyst from the carrier was also examined.

2. Experimental

2.1. Materials

All reactions and manipulations were carried out under inert nitrogen atmosphere. Solvents, toluene and *n*-pentane, were distilled over sodium-benzophenone ketyl before use. Silica (Grace Davison), used as support, had pore volume of $1.5\text{ cm}^3/\text{g}$ and most of the particles had size between 20 and $64\text{ }\mu\text{m}$.

rac-Ethylenebis(1-indenyl)zirconium dichloride, $[\text{rac-Et(Ind)}_2\text{ZrCl}_2]$, trimethylaluminum, and MAO (a 10 wt.% solution in toluene) were obtained from Witco and used as received. Ethylene (grade 3.5 from AGA) and propylene (grade 2.8 from AGA) were further purified by passing through columns filled with molecular sieves, BASF R3-11 catalyst and activated Al_2O_3 or Cu catalyst on Al_2O_3 .

Elemental analyses were conducted with a Carlo Erba Instruments EA 1110 elemental analyzer. Aluminum contents of the modified carriers were determined with X-ray fluorescence (XRF) using a Philips PW 1480 equipment equipped with a Cr anode. Selected samples were also studied with instrumental neutron activation analyses (INAA). In addition, the aluminum and zirconium contents of the carriers 2 and 3 and the heterogeneous catalysts were determined with inductively coupled plasma (ICP) atomic emission spectrometer. Chloride contents were determined by potentiometric titration with AgNO_3 after dissolving the samples into sulfuric acid. The surface areas of the preheated silica samples were checked with BET method with an Omnisorb 100 CX instrument; surface areas were $300\text{ m}^2/\text{g}$ for silicas S1 and S2 and $340\text{ m}^2/\text{g}$ for silica S3.

2.2. Modification of silica

Silica (6 g) was preheated at 350°C (S1 and S2) or at 600°C (S3) for 16 h in a muffle

furnace to control the number and nature of OH groups in the silica. Modified carriers 1, 2, and 3 were prepared from silica samples S1, S2, and S3, respectively. The preheated silica was packed in the ALCVD reactor (F-120C from Microchemistry), where the preheating was continued for 3 h at the same or lower temperature and at low pressure (3–5 kPa) under a nitrogen flow. After heating of the support the TMA precursor was vaporized at room temperature and the vapor was passed through the silica bed at a reaction temperature of 250°C with the aid of nitrogen flow (50 sccm). The duration of the reaction pulse and the amount of precursor needed for saturation were investigated and it was observed that a precursor pulse of 6 h followed by a purge pulse of 2 h was long enough to get an overall saturated surface in the sample bed.

After the reaction the reactor was cooled down and the white modified silica was immediately transferred to a glove box for storage. Three samples from different depths of the carrier bed were taken for XRF analyses to check the uniformity of the aluminum content in the carrier.

2.3. Preparation of the supported catalysts

For *Catalyst 1* was a mixture of *rac*-Et(Ind)₂ZrCl₂, modified carrier 1 and toluene (100 ml) was stirred with a magnetic stirrer at room temperature for an hour and then at 65°C for 7 h. Finally, the mixture was left under stirring overnight. The solid part was separated by filtration and washed four times with 40 ml of toluene and then with 15 ml of pentane. The solvent was removed under vacuum at room temperature. *Catalyst 2* was prepared as catalyst 1 from modified carrier 2, but *rac*-Et(Ind)₂ZrCl₂ was first dissolved in toluene (40 ml) and the dissolved part of the catalyst was added to the reaction mixture with a double-tipped needle. The reaction mixture was then heated at 70°C for 9 h. Catalyst was not washed with pentane.

Catalyst 3 was prepared as catalyst 2 from modified carrier 3, but the reaction mixture was heated at 75°C for 7 h. Pale yellow heterogeneous catalysts were stored under nitrogen in a glove box. Before IR and NMR measurements, samples of heterogeneous catalysts were kept at vacuum for prolonged times (at least 12 h) either at room temperature (catalyst 1) or at 60°C (catalysts 2 and 3) to remove the solvent from the sample.

2.4. FTIR spectra

The supported catalysts and *rac*-Et(Ind)₂ZrCl₂ were characterized under nitrogen atmosphere with the Nicolet Impact 400 D FTIR spectrometer using the diffuse reflectance technique (DRIFT). *rac*-Et(Ind)₂ZrCl₂ was dispersed in dried KBr before the measurement and then measured as a powder like the heterogeneous catalysts as well. The spectrum of a pure KBr was subtracted from the spectrum of metallocene. The spectrometer was equipped with a mercury–cadmium–telluride (MCT) detector. Spectral resolution was 2 cm^{−1} and the spectra were presented in reflectance format.

2.5. NMR spectra

CP MAS NMR measurements of the silica-based samples were carried out with a Bruker AMX-400 FT NMR spectrometer equipped with a magic-angle spinning probehead. The samples were packed in a glove box in ZrO₂ rotors equipped with KEL-F caps. ¹³C CP MAS NMR spectra were measured at 100.61 MHz, with a contact time of 3 ms and a delay of 4 s. In the ²⁹Si CP MAS NMR (79.49 MHz) measurements, the contact time was 5 ms and the delay 5 s. Glycine (NH₂)CH₂COOH (C=O carbon resonating at 176.1 ppm) and adamantane (C₁₀H₁₆) (CH₂ carbons resonating at 38.3 ppm) were used as reference compounds in ¹³C NMR and octa(trimethylsilyl)octasiloxane [(CH₃)₃-

$\text{Si}_8\text{Si}_8\text{O}_{20}$ (resonances of $\text{Si}(\text{CH}_3)_3$ silicons at 11.47 and 11.67 ppm) in ^{29}Si NMR. ^{13}C and ^{29}Si CP MAS NMR spectra were recorded with 20 000 and 18 000 transients, respectively. In the ^1H MAS NMR spectra, water was used as a reference ($\delta_{\text{H}} = 4.80$ ppm) and the number of transients were 800 or 1000. The spinning rate for the 7 mm spinner was 4500 Hz.

The solution ^1H and ^{13}C NMR spectra of *rac*-Et(Ind) $_2\text{ZrCl}_2$ were measured in CDCl_3 . ^{13}C NMR resonances are at 1.7 ($-\text{CH}_2\text{CH}_2-$ bridge), 29.7 (indenyl CH group that is attached to the bridge), and several signals due to indenyl carbons in the area 111–145 ppm. ^1H NMR: 0.111 (bridge hydrogens), 3.80 (indenyl CH group that is connected to the bridge), and the rest indenyl hydrogens were in the area 5.3–7.7 ppm.

2.6. Method of polymerization

The ethylene and propylene polymerization experiments were carried out in 1.0 (unless other mentioned) or 0.5 dm³ stainless steel reactors, respectively. The reactor was evacuated and flushed with nitrogen several times before adding toluene, MAO solution and the suspension of the catalyst in toluene. The total volume of liquid phase was 700 or 300 cm³, respectively. The mixture was stirred and the polymerization reaction was initiated by introducing the monomer. Polymerization temperature and partial pressure of the monomer were kept constant during reaction. The polymer was precipitated with dilute HCl solution in ethanol. The product was isolated by filtering and washed with ethanol.

2.7. Polymer characterization

The molar masses and molar mass distributions of the polymers were determined with a Waters 150-C ALC/GPC gel permeation chromatograph operating at 140°C and equipped with three Waters Styragel columns (HT6, HT4

and HT3) and an RI detector. Solvent 1,2,4-trichlorobenzene was applied at a flow rate of 1.0 cm³/min. The columns were calibrated with narrow molar mass distribution polystyrene standards using a universal calibration method. Linear low density polyethylene and polypropylene standards with known molar mass values were used as references in the selection of Mark–Houwink parameters *K* and α for the samples.

Melting temperatures (T_{m}) and enthalpies (ΔH_{m}) were determined with a Mettler Toledo DSC 821 differential scanning calorimeter. Highly pure indium metal was used for the calibration of the temperature scale. The melting endotherms were measured upon reheating of the polymer sample to 160°C at a heating rate of 10°C/min.

The ^{13}C NMR spectra of polypropylenes were recorded on a Varian Gemini 2000 300 MHz spectrometer at 125°C from samples dissolved in 1,2,4-trichlorobenzene/benzene-*d*₆ (90/10 w/w). The percentage of isotactic triads (mm) was calculated from the signals in the methyl region.

2.8. Catalyst treatment with MAO

Heterogeneous catalyst 1 was treated with methylalumoxane and the Zr content was analyzed after this treatment to examine if the catalyst is desorbed from the carrier due to the cocatalyst. After MAO treatment both the catalyst and the toluene-MAO phase were tested in the polymerization of ethylene.

In this experiment, 18 ml of 10 wt.% MAO was added to mixture of 0.63 g of heterogeneous catalyst 1 and toluene. The mixture was stirred for an hour and then the MAO-toluene solution was filtered away and the remaining catalyst was washed three times with toluene. Solvent was evaporated from the catalyst in vacuum. Furthermore, the filtrate and the first toluene washing solutions (2 × 10 ml) were combined and the MAO-toluene solution was

tested immediately after MAO-treatment in the polymerization so that 60 vol.% of this solution was added into the polymerization reactor.

3. Results and discussion

3.1. Carrier preparation

The modified silica carriers were prepared with ALCVD technique. In this technique, the porous silica surface was modified with vaporized trimethylaluminum at 250°C so that only one molecular layer (monolayer) was formed. The temperature of the substrate controls the adsorption and is high enough to evaporate the physisorbed TMA from the surface. The modification is continued until the surface is saturated with TMA.

The preheating temperature of silica affected the aluminum content of the carriers. Less aluminum was bound to the carrier when the preheating temperature was raised. The carriers 2 (SiO₂ preheated at 350°C) and 3 (SiO₂ preheated at 600°C) contained 4.9 and 3.9 wt.% of aluminum, respectively (Table 1). These values correspond to 3.6 (carrier 2) and 2.6 Al atoms per nanometer square (carrier 3). However, the mole ratio of carbon to aluminum, C/Al, increased from 1.7 (carrier 2) to 2.2 (carrier 3) when the preheating temperature was increased. These observations are consistent with the findings of Lakomaa et al. [10]. The lower ratio of carbon to aluminum in carrier 2 can be explained on the higher amount of –SiOH groups in silica preheated at 350°C. Increase in –SiOH

number leads to a release of carbon as methane from the carrier (reaction A in Scheme 1).

3.2. Adsorption of metallocene onto the support

Metallocene, *rac*-Et(Ind)₂ZrCl₂, was adsorbed on the carrier from a toluene solution at 65–75°C. The amount of zirconium compound used in the synthesis was 1.1–2.0 times greater than the amount of zirconium that was found to bind to the surface. Relatively little zirconium was adsorbed on the carrier, the average value for zirconium content was 0.4 wt.% and the aluminum to zirconium ratio was approximately 40. The mole ratio of chlorine to zirconium, Cl/Zr, was 1.8–1.9 and thus most of the chloride seemed to be left in the carrier (Table 2).

3.3. Characterization of the catalysts

3.3.1. FTIR spectra

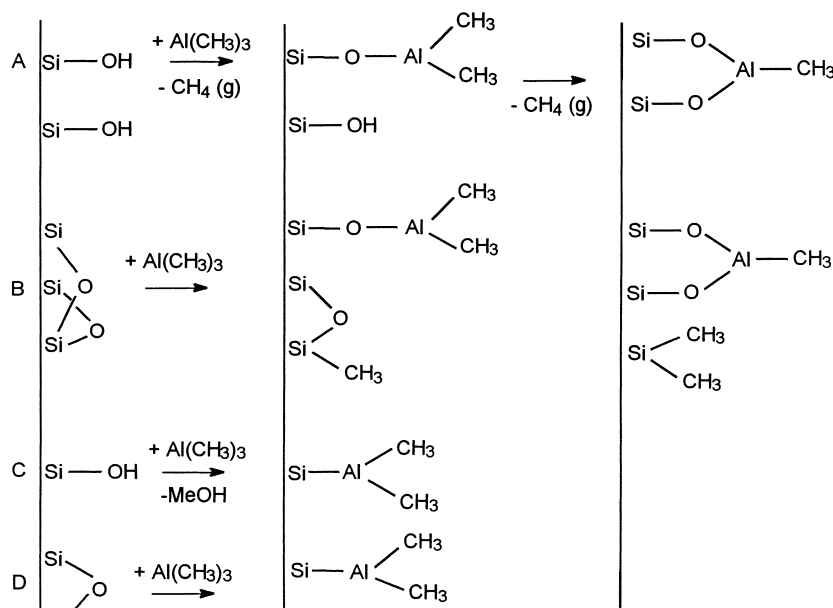
Vansant et al. have [11] summarized the earlier studies on the modification of silica with trimethylaluminum and Scheme 1 illustrates the proposed reactions of TMA with silica. TMA reacts both with the –SiOH groups and the siloxane bridges of the silica with an equal probability [12]. In the reaction with surface silanols, methane is evolved (reaction A in Scheme 1). When TMA reacts with siloxane bridges (reaction B) –SiCH₃ groups are formed. The surface –Al(CH₃)₂ groups can further react with silanol or siloxane groups.

In the FTIR spectrum of modified carrier, the band of isolated –SiOH groups at 3741 cm^{–1} (Fig. 1a) has disappeared. There is, however, a

Table 1
Modification of silica and analyses of TMA/silica carriers

| Carrier no. | <i>T</i> _{preheat} (°C) | <i>T</i> _{modif} (°C) | Al (wt.%) | | C (wt.%) | H (wt.%) | C/Al mole ratio | H/C mole ratio |
|-------------|----------------------------------|--------------------------------|-----------|--------------|----------|----------|-----------------|----------------|
| | | | XRF | ICP | | | | |
| 1 | 350 | 250 | 4.0 | ^a | 3.8 | 1.0 | – | 3.3 |
| 2 | 350 | 250 | 4.6 | 4.9 | 3.6 | 1.1 | 1.7 | 3.6 |
| 3 | 600 | 250 | 3.5 | 3.9 | 3.8 | 0.9 | 2.2 | 2.8 |

^a Not analyzed.



Scheme 1. Suggested reactions of TMA with silica based on reference [11].

broad band in the area $3500\text{--}3700\text{ cm}^{-1}$ indicating that there are hydrogen bonded —SiOH groups left in the carrier. These are probably intraglobular silanol groups, which have a band at 3650 cm^{-1} [11] and are inside the silica structure unable to react with TMA.

The C—H stretching vibrations of CH_3 groups are at 2960 , 2940 (shoulder), 2902 , and 2833 cm^{-1} in the carrier spectra. These bands have been assigned in the literature [11] to —SiMe groups (2960 and 2902 cm^{-1}) and —AlMe groups (2940 , 2902 , and 2833 cm^{-1}). In addition, the possible methoxy groups have

been reported to have bands at 2860 , 2960 and 3000 cm^{-1} [11]. On the basis of carrier IR spectra there are no methoxy groups in the carriers because the bands at 2860 and 3000 cm^{-1} are missing.

In the FTIR spectra of catalysts, changes can be seen. A new weak shoulder arises at 2860 cm^{-1} , this band belongs to the adsorbed Zr compound (see Fig. 1b). The $\text{rac-Et(Ind)}_2\text{Zr-Cl}_2$ complex (Fig. 1c) has one C—H stretching vibration of the $\text{—CH}_2\text{CH}_2\text{—}$ bridge at 2865 cm^{-1} . Moreover, in the IR spectra of heterogeneous catalysts, there are new weak $\nu(\text{C—H})$ bands of

Table 2

Preparation and analyses of heterogeneous $\text{rac-Et(Ind)}_2\text{ZrCl}_2/\text{TMA}/\text{SiO}_2$ catalysts

| Catalyst no. | Amount of carrier (g) | Amount of Zr compound (mg) | Amount of Cl (wt. %) | Al (wt. %) | Zr (wt. %) | Al/Zr mole ratio | Cl/Zr mole ratio |
|--------------|-----------------------|----------------------------|----------------------|------------|------------|------------------|------------------|
| 1 | 3.00 | 65.6 | ^a | 4.5 | 0.45 | 34 | — |
| 2 | 1.27 | 43.0 | 0.25 | 4.5 | 0.35 | 44 | 1.8 |
| 3 | 1.92 | 42.5 | 0.28 | 3.7 | 0.38 | 33 | 1.9 |

^a Not analyzed.

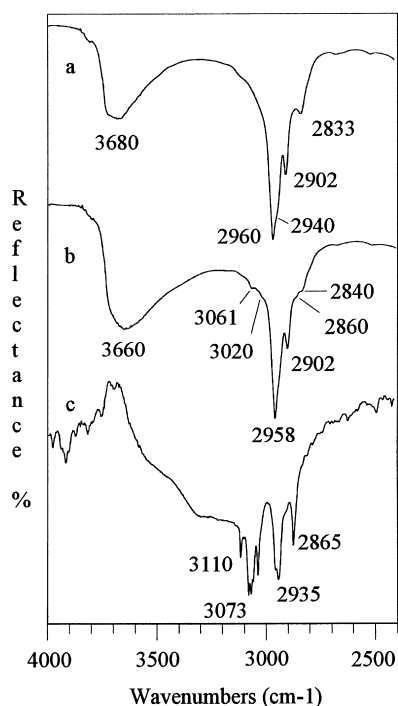


Fig. 1. FTIR spectra of (a) trimethylaluminum treated silica carrier 3; (b) corresponding heterogeneous catalyst 3; (c) spectrum of *rac*-Et(Ind)₂ZrCl₂ complex (in KBr).

the indenyl ligands at 3020 and 3060 cm⁻¹. The homogeneous Zr compound has several bands due to indenyl ligand above 3000 cm⁻¹.

The signal of -AlCH_3 groups near 2840 cm⁻¹ has diminished in size in the IR spectrum of the catalyst. Moreover, the shoulder at 2940 cm⁻¹ due to -AlCH_3 groups is no longer visible in the catalyst spectrum indicating that -AlCH_3 groups have reacted with metallocene.

3.3.2. MAS NMR spectra

According to the best of our knowledge there are only few detailed MAS NMR studies on TMA modified silica materials. The study of Lakomaa et al. [10] dealt with the layer by layer growth of Al₂O₃ from TMA and water vapor on silica using ALE technique, while Anwender et al. [13] studied the Lewis acidity of TMA treated purely siliceous MCM-41 material. Moreover, there is, for example, the investiga-

tion on the hydrolysis of TMA on MCM-41 by Van Looveren et al. [14].

3.3.2.1. ¹³C NMR. In the ¹³C CP MAS NMR spectrum (Fig. 2a) of a TMA modified silica, the broad resonance at -11 to -13 ppm belongs to -AlCH_3 carbons. For comparison, in the literature the chemical shift of -AlCH_3 groups on the carrier is in the area -7.4 to -9.5 ppm [13,14]. The intensity of this signal diminished after adsorption of the metallocene on the TMA/SiO₂ carrier and indicates that -AlCH_3 groups reacted with metallocene. The change in intensity was obvious in the spectra of catalysts 1 (Fig. 2a) and 3, but insignificant between carrier 2 and catalyst 2. The strongest signal in the ¹³C NMR spectra belongs to $(\text{-O})_2\text{SiMe}_2$ groups, which have a signal at -0.8 ppm. Spectral simulation was needed to

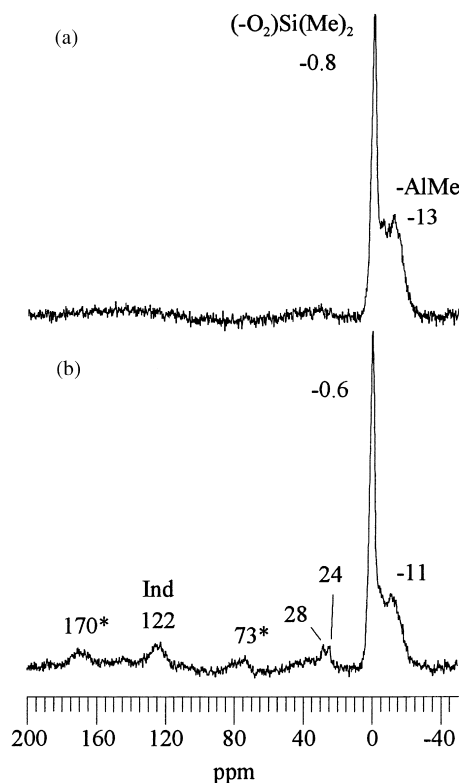


Fig. 2. ¹³C CP MAS NMR spectra of (a) trimethylaluminum treated silica carrier 1; (b) corresponding catalyst 1. Asterisk denotes a spinning side band.

distinguish the carbons of $(-\text{O})_3\text{SiMe}$ and $-\text{OSiMe}_3$ groups, which exists on the basis of ^{29}Si NMR measurements. The ^{13}C NMR signal of $(-\text{O})_3\text{SiMe}$ group is near -4 ppm and $-\text{OSiMe}_3$ groups have a weak signal near 2 ppm. In the study of Lakomaa et al. [10], $(-\text{O})_3\text{SiMe}$ signal was distinguished after treatment of the carrier with water, which caused the disappearance of $-\text{AlMe}$ groups. In the reaction of TMA with SiO_2 at 250°C , no methoxy groups are formed because the ^{13}C NMR spectra of carriers did not contain a signal of methoxy groups which have been reported at 50 – 60 ppm [10,13]. On this basis, the reaction D presented in Scheme 1 does not occur in the TMA modification of SiO_2 using ALCVD method.

The relative amounts of $-\text{SiMe}$ and $-\text{AlMe}$ groups can be estimated from the simulated ^{13}C NMR spectrum. Based on the simulated ^{13}C NMR results, about 40% of the methyl groups are in $-\text{AlMe}$ species in a TMA/ SiO_2 carrier that was prepared from silica preheated at 600°C . This value suggests a $-\text{SiMe}/-\text{AlMe}$ ratio of 1.5 and similar relation was obtained from simulated ^1H MAS spectrum. Carrier 3 (SiO_2 preheated at 600°C) contained more $-\text{SiMe}$ groups than carrier 1 (SiO_2 preheated at 350°C). Except this difference, the $-\text{SiMe}/-\text{AlMe}$ distribution was at a rough estimate similar in both carriers. Carrier 2 differed from other carriers in that the intensity of the $-\text{AlMe}$ signal was higher than in other carriers. When in addition to the $-\text{SiMe}/-\text{AlMe}$ ratio, the ratio of carbon to aluminum (2.2 in carrier 3) is considered, an obvious conclusion is that in the carrier may also be $\text{Al}(\text{O}-)_3$ aluminum sites that have no methyl groups left.

Anwander et al. [13] have reported a methyl surface population with a $-\text{SiMe}/-\text{AlMe}$ ratio of 0.45 . In their experiment, silica was treated with TMA at ambient temperature. In our case, the higher ratio (1.5) is probably due to higher chemisorption temperature, which means that the carrier does not contain physisorbed TMA and the surface $-\text{AlCH}_3$ groups can react further so that more $-\text{SiCH}_3$ groups are formed.

In the ^{13}C CP MAS NMR spectrum of the catalyst 1 (Fig. 2b), there is a broad resonance of the indenyl ligand at 122 ppm with spinning sidebands at 73 and 170 ppm in the aromatic carbon area. In the spectra of catalyst 1, the weak band at 28 ppm belongs to the indenyl carbons that are connected to $-\text{CH}_2\text{CH}_2$ -bridge, because the $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ compound has this signal at 30 ppm. The weak signal at 24 ppm could belong to $-\text{ZrMe}$ moiety and is discussed later in the context of ^1H NMR spectra.

3.3.2.2. ^{29}Si NMR. ^{29}Si NMR spectrum of carrier 3 in Fig. 3 shows that there are, in addition to siloxane bridges at -107 ppm, three different types of silicon species present in the carrier: these are the $(-\text{O})_3\text{SiMe}$, $(-\text{O})_2\text{SiMe}_2$, and $-\text{OSiMe}_3$ groups which resonate at -60 , -7 , and 23 ppm, respectively [10]. The increase in the preheat temperature of SiO_2 enhanced the

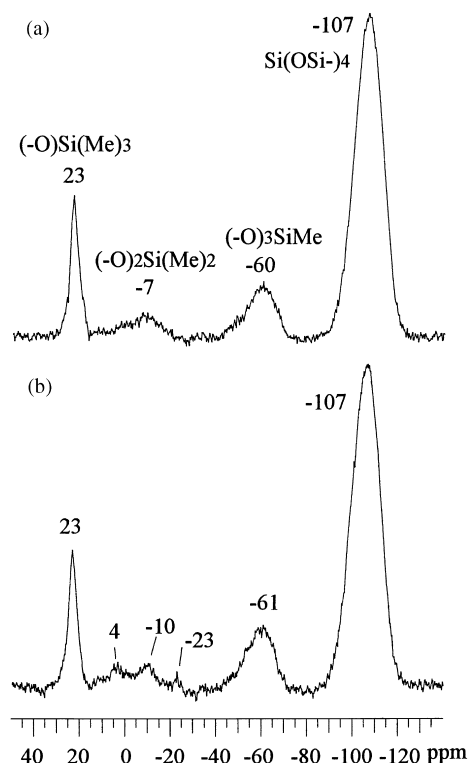


Fig. 3. ^{29}Si CP MAS NMR spectra of (a) carrier 3; (b) heterogeneous catalyst 3.

amount of $-\text{OSiMe}_3$ groups, because the intensity of the $-\text{OSiMe}_3$ signal in the spectrum of carrier 3 was higher than in other carriers. The $-\text{SiOH}$ group silicons resonate at about -100 ppm [11]. Because this resonance is not distinguished in the carrier spectra, the number of $-\text{SiOH}$ groups left in the carrier after TMA treatment is very small and the remaining $-\text{SiOH}$ groups are probably inside the silica structure. We did not have reference data on ^{29}Si chemical shifts of silicon compounds that have a $\text{Si}-\text{Al}$ bond, so the reaction C in Scheme 1 can not be excluded.

Replacement of OSi moiety with OAl moiety in $\text{Si}(\text{OSi}-)_4$ groups shifts the resonance of the siloxane silicons (at -109 ppm in SiO_2 [11]) to lower field depending on the number of aluminum atoms surrounded by the silicon [15]. For example, the $\text{Si}(\text{OSi}-)_3(\text{OAl}-)$ silicons have been reported to resonate in the area -97 to -107 ppm in aluminosilicates and correspondingly $\text{Si}(\text{OSi}-)_2(\text{OAl}-)_2$ and $\text{Si}(\text{OSi}-)(\text{OAl}-)_3$ silicons in the area -92 to -100 ppm and -85 to -94 ppm , respectively [15]. These groups are not visible in the carrier spectra but the broad resonance at -107 ppm assigned to siloxane bridges, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$, can contain $\equiv\text{Si}-\text{O}-\text{Al}\equiv$ groups as well. One reason for the small intensity of the resonance of the $\equiv\text{Si}-\text{O}-\text{Al}\equiv$ groups in the carrier is probably the used $^1\text{H}-^{29}\text{Si}$ cross-polarization technique, where the proximity of the hydrogen is needed before silicon atoms can be seen in the spectra and the distance between silicon and hydrogen atoms affects the intensity of the NMR signal. For this same reason, ^{29}Si and ^{13}C CP MAS NMR spectra are not quantitative [15].

3.3.2.3. ^1H NMR. The ^1H MAS NMR spectra of carrier 3 and the corresponding catalyst 3 are in Fig. 4. In the ^1H NMR spectra of carriers, there is one broad signal at 0 to -0.1 ppm , which belongs to $-\text{SiMe}$ groups. For reference, the signal of $-\text{SiMe}$ groups has been reported at 0.2 ppm [13]. The $-\text{AlCH}_3$ signal is not well resolved in carrier spectra, but the spectral sim-

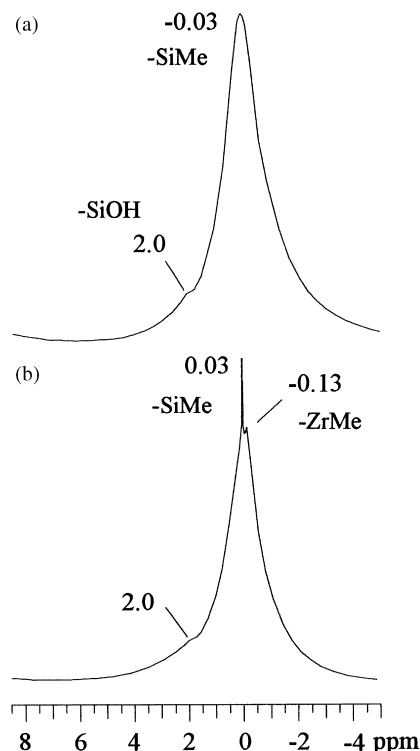
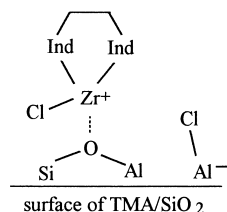


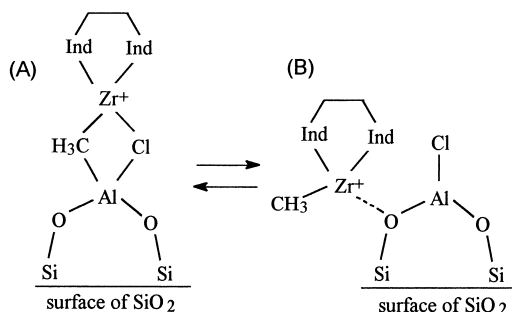
Fig. 4. ^1H MAS NMR spectra of (a) carrier 3; (b) catalyst 3.

ulation gives a broad signal at -0.5 ppm . This value is near the chemical shift of $-\text{AlCH}_3$ groups reported at -0.6 ppm [13]. In the carrier spectra, a broad shoulder at 2 ppm and a narrower weak signal around 1.5 ppm (missing from carrier 3) belong to $-\text{SiOH}$ groups [16]. For reference, the chemical shift of the $-\text{SiOH}$ signal has been reported at 1.7 – 2.0 ppm [13,17]. After adsorption of metallocene onto the carrier, the $-\text{CH}_3$ signal in the spectrum of catalyst 3 was narrower, when comparing with the spectrum of carrier 3, indicating that part of the $-\text{CH}_3$ groups had reacted. Changes between the ^1H NMR spectra of other carriers and catalysts were smaller. Additionally, a new weak ^1H resonance was distinguished at -0.13 to -0.18 ppm in the spectra of all catalysts. New signal could be due to either terminal or bridging methyl group attached to Zr. Two structures (A and B) for surface species containing $-\text{ZrMe}$ group are presented in Scheme 2. For reference,

(a) Abstraction



(b) Exchange reaction



Scheme 2. Suggested mechanism for adsorption of metallocene on TMA treated SiO_2 surface. (a) Halide abstraction by a Lewis acidic aluminum and coordination of cationic complex to the surface. (b) Exchange reaction between cationic complex and surface $(-\text{O})_2\text{AlMe}$ group.

rac- $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ has the chemical shift δ_{H} of methyl group at -1.42 ppm [18]. In the cationic complex, this signal is shifted to lower field due to electron deficient Zr center. Replacement of methyl group with chlorine also shifts the signal to lower field.¹ The cationic $[\text{Et}(\text{Ind})_2\text{ZrMe}]^+[\text{MAO}]^-$ has $-\text{ZrMe}$ signal at -0.67 ppm while $[\text{rac-Et}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ has $\text{Zr}-(\mu\text{-Me})-\text{Al}$ signal at -0.63 ppm [18]. Methyl bridge in $\text{Zr}-(\mu\text{-Me})-\text{Zr}$ system, instead, has signals in higher field at ca. -3 ppm in $\{[\text{Et}(\text{Ind})_2\text{ZrMe}]_2(\mu\text{-Me})\}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ [20]².

¹ For comparison, Kaminsky et al. [19] report the ^1H NMR signals of Me groups for $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ ($\delta_{\text{H}} = 0.44$) and for $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ ($\delta_{\text{H}} = -0.13$).

² ^1H NMR (CD_2Cl_2 , -60°C): $\delta = -0.87$ and -0.96 (terminal Me), $\delta = -2.99$ and -3.10 ($\mu\text{-Me}$) for two isomers of $\{[\text{Et}(\text{Ind})_2\text{ZrMe}]_2(\mu\text{-Me})\}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. NMR (CD_2Cl_2): $\delta_{\text{C}} = 37.3$ and $\delta_{\text{H}} = -0.63$ for ($\mu\text{-Me}$) in $[\text{Et}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$.

And it is not probable that the new signal approximately at -0.15 ppm would be due to this latter system.

On the other hand, $-\text{ZrMe}$ signal should be visible in the ^{13}C NMR, too. In the catalyst spectrum in Fig. 2b, there is one unassigned signal at 24 ppm, which suits well for the chemical shift of bridging methyl group in dimeric cation like $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Me})]^+[\text{MeMAO}]^-$ [21]³. However, both terminal ($-\text{ZrMe}$) and bridging ($\text{Zr}-\text{Me}-\text{Al}$) methyl groups in cationic complexes have chemical shifts usually near 40 ppm [21,22], but this signal is missing from ^{13}C NMR of catalysts. It seems that the new resonances in ^1H and ^{13}C NMR spectra of our catalyst belong to a $-\text{ZrMe}$ species, the structure of which remains unresolved.

3.4. Catalyst structure

When metallocene was adsorbed on the carrier at least part of the Zr species on the carrier reacted with $-\text{AlMe}$ groups because their amount was reduced judged on the basis of ^{13}C NMR and FTIR spectra of the catalysts. Furthermore, in the ^1H NMR spectra of catalysts a new signal, which could belong to $-\text{ZrMe}$ groups, arised near -0.15 ppm.

The existence of Lewis acidic sites on TMA/ SiO_2 carrier has been reported [13,22,23]. Panchenko et al. [22] have stated that there are two types of Lewis acidic sites on trimethylaluminum treated silica surface, the concentration of these sites was, however, low. Additionally, they reported that the amount of adsorbed metallocene corresponded the amount of Lewis acidic sites.

The surface aluminum species are assumed to be three-coordinated, coordinatively unsaturated

³ For comparison ^{13}C NMR (toluene- d_8 , -20°C): δ of terminal Me group at 40.7 for $[\text{Cp}_2\text{ZrMe}]^+[\text{MeMAO}]^-$ and 22.5 ($\mu\text{-Me}$) and 39.8 ($\text{Zr}-\text{Me}$) for $[(\text{Cp}_2\text{ZrMe})_2(\mu\text{-Me})]^+[\text{MeMAO}]^-$.

electron deficient species which makes them Lewis acidic. If the amount of adsorbed zirconium corresponds the amount of Lewis acidic sites, the high aluminum to zirconium ratio (ca. 40), suggests that only small part of the surface aluminum acts as Lewis acid. One possible reason to this could be π -bonding interaction of the empty p-orbital of aluminum with the lone pairs of closely oxygen, that would explain the change in Lewis acidity of aluminum.

3.5. Polymerization experiments

The prepared heterogeneous catalysts 1, 2 and, 3 were tested in the polymerization of ethylene and propylene in the presence of methylalumoxane using different polymerization temperatures and aluminum to zirconium ratios. The melting temperatures, molar masses and molar mass distributions of the polymer samples were also determined.

Polymerization results with ethylene are reported in Table 3. The activities of both heterogeneous and the corresponding homogeneous

catalyst were highly dependent on the polymerization temperature and the Al/Zr-ratio, although the activities of the heterogeneous catalysts were much lower than the activity of the homogeneous catalyst. Highest obtained activities were 243 000 kg of PE/(mol Zr \times h) for homogeneous *rac*-Et(Ind)₂ZrCl₂ (catalyst no. 4), 7400 kg of PE/(mol Zr \times h) for heterogeneous catalyst 1, 17 000 kg of PE/(mol Zr \times h) for catalyst 2 and 31 000 kg of PE/(mol Zr \times h) for catalyst 3. The activities decreased in order homogeneous catalyst 4 \gg catalyst 3 > catalyst 2 > catalyst 1 at 80°C.

The properties of polyethylenes prepared with heterogeneous or homogeneous catalysts were rather similar. Molar masses of polymers prepared with supported catalysts at 50°C were lower than molar masses of PEs prepared with the corresponding homogeneous catalyst. This is, however, presumably due to a difference in the rates of ethylene consumption during polymerization, which may have an impact on the concentration of monomer in the reaction medium. The measured melting temperatures of

Table 3

Polymerizations of ethylene with heterogeneous catalysts and homogeneous catalyst^a

| Catalyst no. | Experiment | n_{Zr} (μmol) | Al/Zr | T_p (°C) | t_p (min) | Yield (g) | A^b | T_m (°C) | \bar{M}_w (g/mol) | \bar{M}_w/\bar{M}_n |
|----------------|------------|-------------------------------------|-------|------------|-------------|-----------|--------|------------|---------------------|-----------------------|
| 1 | a | 1.0 | 2000 | 50 | 30 | 2.8 | 5700 | 137.2 | 136000 | 2.2 |
| | b | 5.1 | 500 | 80 | 30 | 5.5 | 2100 | 133.2 | 91000 | 2.2 |
| | c | 3.2 | 1000 | 80 | 30 | 6.5 | 4100 | 133.8 | 89000 | 2.2 |
| | d | 1.0 | 2000 | 80 | 30 | 3.7 | 7400 | 133.9 | 75000 | 2.0 |
| 2 | a | 8.0 | 2000 | 30 | 30 | 1.1 | 270 | 134.1 | 207000 | 2.7 |
| | b | 2.0 | 1000 | 50 | 33 | 1.2 | 1100 | 137.0 | 142000 | 2.2 |
| | c | 1.0 | 2000 | 50 | 30 | 1.3 | 2600 | 135.8 | 132000 | 2.1 |
| | d | 10.5 | 250 | 80 | 10 | 6.1 | 3500 | 133.3 | 91000 | 2.2 |
| | e | 3.2 | 1000 | 80 | 10 | 4.6 | 8700 | 133.0 | 85000 | 2.1 |
| | f | 1.0 | 2000 | 80 | 30 | 8.5 | 17000 | 132.9 | 88000 | 2.0 |
| 3 | a | 3.3 | 1000 | 80 | 30 | 29.1 | 18000 | 133.4 | 109000 | 2.3 |
| | b | 1.0 | 2000 | 80 | 30 | 14.9 | 30000 | 133.3 | 94000 | 2.1 |
| | c | 3.2 | 2000 | 80 | 10 | 16.3 | 31000 | 133.3 | 81000 | 1.9 |
| 4 ^c | a | 1.8 | 1000 | 30 | 10 | 5.3 | 18000 | 136.8 | 235000 | 2.5 |
| | b | 3.0 | 500 | 50 | 10 | 5.1 | 10000 | 136.0 | 186000 | 2.5 |
| | c | 0.8 | 2000 | 50 | 20 | 11.6 | 44000 | 136.2 | 198000 | 2.7 |
| | d | 0.7 | 2000 | 80 | 1.5 | 4.3 | 243000 | 135.3 | 70000 | 1.8 |

^a Ethylene overpressure 1.5 bar, reactor 1.0 dm³.

^b Activity of catalyst in kg of PE/(mol of Zr \times h).

^c Homogeneous catalyst.

Table 4

Polymerizations of propylene with heterogeneous catalysts and homogeneous catalyst^a

| Catalyst no. | Experiment | n_{Zr} (μmol) | Al/Zr | t_p (min) | Yield (g) | A^b | T_m ($^{\circ}\text{C}$) | M_w (g/mol) | M_w/M_n | [mm]% |
|----------------|------------|-------------------------------------|-------|-------------|-----------|-------|------------------------------|---------------|-----------|-------|
| 1 | a | 9.8 | 2000 | 60 | 7.6 | 770 | 138.8 | 41000 | 2.0 | 93.4 |
| 3 | a | 30.0 | 1000 | 30 | 5.1 | 340 | 139.2 | 36000 | 1.9 | |
| 4 ^c | a | 2.0 | 500 | 30 | 11.6 | 12000 | 138.3 | 44000 | 2.0 | |
| | b | 2.0 | 1000 | 30 | 33.1 | 33000 | 137.6 | 43000 | 2.0 | |
| | c | 2.0 | 2000 | 30 | 30.8 | 31000 | 137.6 | 42000 | 1.9 | 93.2 |

^a Propylene overpressure 3 bar, temperature 30 $^{\circ}\text{C}$, reactor 0.5 dm³.^b Activity of catalyst in kg of PP/(mol of Zr \times h).^c Homogeneous catalyst.

PEs were between 133 and 137 $^{\circ}\text{C}$ depending on the temperature in which the polymerizations were performed. Heat of fusion of the prepared polymers varied between 150 and 220 J/g depending on the activity and the amount of catalyst used. These are typical values of linear or slightly branched PEs [24].

Polymerization results with propylene are presented in Table 4. Heterogeneous catalysts also polymerized propylene but with lower activity than the homogeneous catalyst. The activities varied between 340 and 770 kg of PP/(mol Zr \times h). The activities of homogeneous catalyst in same polymerization conditions varied from 33 000 to 37 000 kg of PP/(mol Zr \times h). The PPs prepared with supported catalysts 1 or 3 and the homogeneous catalyst 4 were similar in melting temperatures and molar masses. No difference in the tacticity of polymers was observed by ¹³C NMR.

Higher preheating temperature of the silica carrier seemed to improve the activity of the heterogeneous catalyst. According to FTIR, ¹³C and ²⁹Si NMR measurements, the carriers 1 (silica preheated at 350 $^{\circ}\text{C}$) and 3 (silica preheated at 600 $^{\circ}\text{C}$) had fairly similar NMR spectra, so they do not give any explanation for different activities. One reason for the better activity of catalyst 3 could be based on the ¹H NMR results. Because the spectrum of catalyst 3 indicated that part of the methyl groups had reacted with metallocene.

3.6. Catalyst treatment with MAO

Leaching of the catalyst from the carrier was examined by treating catalyst 1 with MAO in toluene solution at room temperature. In this experiment, the mole ratio of aluminum to zirconium was 950. Polymerization results with

Table 5

Treatment of catalyst 1 with MAO: zirconium contents and ethylene polymerization results before and after treatment^a

| Catalyst no. | Zr (wt.%) | catalyst (mg) | Al/Zr | t_p (min) | Yield (g) | A^b | T_m ($^{\circ}\text{C}$) | M_w (g/mol) | M_w/M_n |
|-----------------------|-----------|---------------|-------|-------------|-----------|-------------------|------------------------------|---------------|-----------|
| 1 | 0.45 | 199 | — | 30 | 0 | — | | | |
| 1 | 0.45 | 100 | 500 | 60 | 1.6 | 324 | | | |
| 1 | 0.45 | 97 | 1000 | 35 | 3.6 | 747 | 134.4 | | |
| MAO/1 ^c | 0.30 | 98 | 1500 | 60 | 0.6 | 180 | 134.2 | 273000 | 2.6 |
| Filtrate ^d | | | | 30 | 4.4 | 1400 ^e | 135.4 | 275000 | 2.4 |

^a Polymerization conditions: 0.5 dm³ reactor, temperature 30 $^{\circ}\text{C}$, ethylene overpressure 2 bar, stirring speed 400 rpm.^b Activity of catalyst in kg of PE/(mol of Zr \times h).^c Catalyst 1 after treatment with MAO and washing with toluene.^d 60 vol.% of the MAO-toluene filtrate was used in polymerization.^e The Zr content of the filtrate is estimated on the basis of the Zr content of MAO treated catalyst.

the filtrate and the treated heterogeneous catalyst and zirconium contents of the catalyst after and before the MAO treatment are reported in Table 5. One third of the zirconium was desorbed from the carrier and the resulting solution containing the leached catalyst had relatively high activity. Similar leaching problems have been reported earlier [25,26].

One polymerization experiment was conducted without any added cocatalyst using catalyst 1. No polymer was found in the reactor after polymerization, so an additional cocatalyst is needed at least to scavenge impurities from the reactor. The use of trialkylaluminum alkyls, such as tri-isobutylaluminum (TIBA) could possibly solve the leaching problem of heterogeneous catalyst, because the leached metallocene has been reported not to be active if TMA or TIBA is used as a cocatalyst [1,26].

4. Conclusions

ALCVD (also called as ALE) technique is an alternative method to prepare supported metallocenes. The silica surface was treated with vaporized trimethylaluminum until the surface was saturated. When this was done at 250°C $-\text{SiCH}_3$, $-\text{Si}(\text{CH}_3)_2$, $-\text{Si}(\text{CH}_3)_3$, and monomethylaluminum, $=\text{AlCH}_3$, surface species were formed. Enhance in the preheat temperature of SiO_2 increased the amount of $-\text{OSi}(\text{CH}_3)_3$ groups and reduced the content of aluminum of the carrier. Regarding the low ratio of carbon to aluminum (2.2 in carrier 3) and that about 60% of all the methyl groups were bonded to the surface as $-\text{SiCH}_3$ groups, it is possible that part of the aluminum atoms lost all their methyl groups and $\text{Al}(\text{O}-)_3$ groups were formed. The formed three-coordinated Al species are possible adsorption sites for the metallocene.

Heterogeneous catalysts were synthesized by adsorbing the metallocene, $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$, onto the TMA modified silica in toluene. The amount of $-\text{AlMe}$ groups diminished after ad-

sorption of the metallocene onto the surface and in the ^1H and ^{13}C MAS NMR a new signal possibly due to $-\text{ZrMe}$ groups arose. Relatively low concentration of Zr on the carrier, the ratio of aluminum to zirconium being about 40, suggests that only part of the aluminum sites act as suitable adsorption sites for the metallocene.

Heterogeneous $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2/\text{TMA}/\text{SiO}_2$ catalyst produced similar polymer as the corresponding homogeneous catalyst in the presence of MAO, but with lower activity. Heterogeneous catalysts were not active without additional cocatalyst in the polymerization. Added methylalumoxane cocatalyst, however, caused desorption of part of the zirconium species from the carrier and the leached catalyst had relatively high activity.

This study has shed light on the adsorption sites that are formed when silica is treated with trimethylaluminum. Despite intensive study, the development of heterogeneous catalysts is still at an early stage and further research is needed before we understand the interactions between metallocene and the carrier. An ideal catalyst, where all the good properties of the heterogeneous catalysts would combine, remains the goal of future research.

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