

Study of the supported zirconocene catalysts by means of UV/vis and DRIFT spectroscopy

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Abstract

UV/vis in diffusion reflection mode (DRS) and DRIFT spectroscopy have been used to study the surface zirconocene species formed at the interaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ complexes with the MAO/SiO₂ support. Effect of additional activation of these catalysts with TIBA has been studied as well.

Structure of type $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}]^+[\text{MeMAO}]^-$ (C) is formed at the reaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ complex with MAO/SiO₂ (a.b. at 456 nm in UV/vis spectra). Interaction of this complex with TIBA results in the formation of new structure (D) with a.b. at 496 nm in UV/vis spectra.

The surface species of different composition and structures are formed at interaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ complex with MAO/SiO₂. The ratio between these species depends on the zirconium content in the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalysts. According to the DRIFTS data (CO and ethylene adsorption) and ethylene polymerization data these catalysts contain active Zr–Me bonds but activity of these catalysts at ethylene polymerization is low. Interaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ with TIBA leads to the formation of the new cationic structure of type (D) with a.b. at 496 nm in UV/vis spectra and great increasing of activity at ethylene polymerization.

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1. Introduction

Metallocenes being used in combination with suitable activating agents (polymethylalumoxane (MAO) or perfluoroarylborate activators (FAB)), are highly active catalysts for alkene polymerization [1,2]. For practical applications, supported metallocene catalysts are considered as the most promising. One of the most effective ways to synthesize these catalysts consists in supporting metallocene complexes on silica modified with methylalumoxane (MAO/SiO₂) [3,4].

In spite of great interest in supported metallocene catalysts, few papers are devoted to the study of the surface zirconium species in zirconocene/MAO/SiO₂ catalysts [5–9].

Most studies focus mainly on the kinetics of polymerization and molecular structures of the polymers [3,4,10,11].

Earlier we have studied the interaction of MAO with silica by IRS [6]. It has been shown that MAO freed from excess of free AlMe_3 adsorbs mainly on the surface OH-groups of silica without noticeable protolytical reaction. When the silica is treated with commercial grade MAO with significant TMA content, the surface OH-groups of silica interact mainly with TMA, while MAO adsorbs on the surface of silica, which contains surface groups of the type $(\equiv\text{Si}-\text{O})_n^- \text{AlMe}_{3-n}$ groups ($n = 1, 2$). The acidity of the MAO/SiO₂ support has been studied by IRS (adsorption of CO as probe molecule) [6]. Two types of the Lewis acidic sites (LAS) were found on the surface of MAO/SiO₂ support: LAS-M of moderate strength ($\nu_{\text{CO}} = 2204\text{--}2212\text{ cm}^{-1}$) and weak LAS-W ($\nu_{\text{CO}} = 2194\text{ cm}^{-1}$). Cp_2ZrMe_2 was shown by IRS methods to interact both with the LAS-W and LAS-M acidic sites [5]. A correlation between the amount of LAS-M and activity with

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respect to ethylene polymerization has been found as well [5]. Later we have studied by IRS methods also the interaction of carbon monoxide with catalyst $\text{Cp}_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ [12]. We have found that a σ -carbonyl complex of zirconocene with CO ($[\text{Cp}_2\text{Zr}(\text{Me})(\text{CO})]^+$, $\nu_{\text{CO}} = 2146 \text{ cm}^{-1}$) is formed at 77 K by the $\text{Cp}_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ catalyst. At room temperature, this complex is transformed to the acyl complex via insertion of CO into the Zr–Me bond [12].

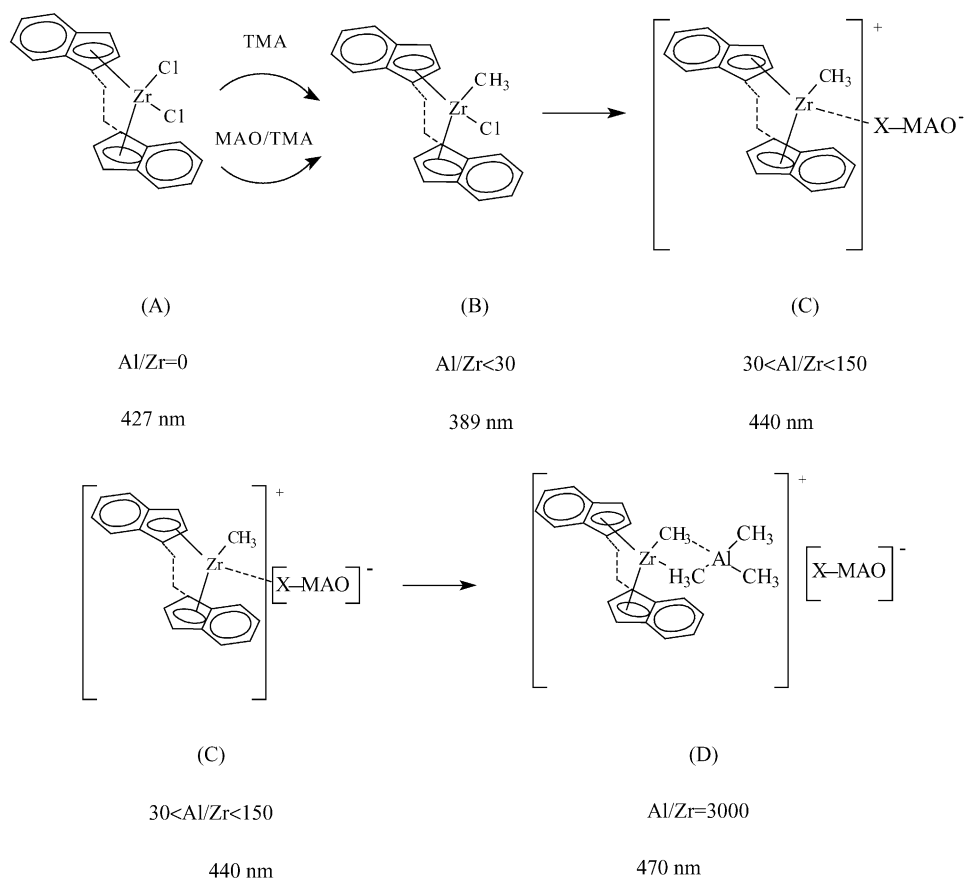
Composition and structures of intermediates formed in homogeneous zirconocene catalysts upon activation with MAO have been studied by means of ^{13}C -NMR spectroscopy [13–15]. According to these data highly polarized and ionic intermediates of various composition are formed at various MAO/Zr ratios. In particular, complexes of type $\text{L}_2\text{ZrMe}^+ \leftarrow \text{Me-MAO}^-$ (I) and $[\text{L}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+ [\text{Me-MAO}]^-$ (II) are formed at different Al/Zr ratios ($\text{L} = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{H}_5\text{-}_n$ – R_n and Me_2Si -bridged indenyl ligands).

In recent years, UV/vis spectroscopy has been used for the investigation of homogeneous zirconocene/MAO systems [16–19,21]. This method proved to be a useful instrument for the monitoring of homogeneous zirconocene/MAO systems at different steps of the activation process. NMR and UV/vis literature data [14–19,21] (Scheme 1) indicate that formation

of monomethylated zirconocene (B) at low Al/Zr ratios (up to 30) is associated with a hypsochromic shift of the initial metallocene absorption band from 427 nm (complex A) to 389 nm (complex B). A bathochromic shift of the absorption band in two distinct steps is observed when MAO/Zr ratios are increased from 30 to 2000. By these processes “cationic” species of types (C) and (D) (440 and 470 nm, Scheme 1) are formed, which have also been identified by NMR spectroscopy [13–15]. Species of type (C) appeared to be inactive for hexene-1 polymerization [16–18], when a too strongly coordinating anion X-MAO^- is in contact with their Zr center.

While UV/vis spectroscopy effectively allows to study the activation processes induced by interaction of MAO with zirconocene in homogeneous systems, only one publication [20] deals with the activation of a supported catalyst, hafnocene/MAO/SiO₂, by means of UV/vis techniques.

In the present paper we report studies on surface zirconocene species formed upon interaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ complexes with a MAO/SiO₂ support by means of UV/vis spectroscopy in diffusion reflection mode (DRS). Additional activation of these catalysts with TIBA has been studied as well by means of UV/vis spectroscopy.



Scheme 1. Possible structures of zirconocene species formed at interaction of $(\text{En})(\text{Ind})_2\text{ZrCl}_2$ zirconocene complex with MAO [16–19].

2. Experimental

All experiments were performed under vacuum or argon atmosphere using the “break-seal” technique.

Silica Davison 952 (surface area 260 m²/g) has been used as a support. Methylaluminoxane from Witco was used as a toluene solution (total Al content 1.8 M, Al as Al(CH₃)₃ 0.5 M).

Me₂Si(Ind)₂ZrCl₂ and Me₂Si(Ind)₂ZrMe₂ were synthesized according to literature reports [22,23].

2.1. Synthesis of support

A sample of 5 g of silica was heated in air at 500 °C for 3 h, then placed into a quartz ampoule and dehydroxylated in a dynamic vacuum at 800 °C for 3 h. Then it was treated with 50 ml of 0.18 M solution of MAO in toluene ([Al]/[Si–OH] = 15). The suspension thus obtained was stirred at 20 °C for 0.5 h. The reaction products and residual aluminum compounds were washed with toluene (three times). The modified supports were dried at room temperature under vacuum for 1 h. The support thus obtained contains 15 wt.% of aluminum.

2.2. Catalysts preparation

Catalysts were prepared by treatment of the support with measured amounts of a toluene solution of Me₂Ind₂ZrCl₂ or Me₂Si(Ind)₂ZrMe₂ to provide the desired Zr content. Catalysts were dried in vacuum without previous washings.

Catalysts Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ and Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ containing 0.1 wt.% of Zr were treated with a heptane solution of Al(*i*-C₄H₉)₃ (TIBA) at different Al_{TIBA}/Zr ratios at 20 °C. Then the samples were dried in vacuum without previous washing.

2.3. Chemical composition

The aluminum content in the samples has been determined by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.4. UV/vis studies

Samples of supports and catalysts were placed, in form of dry powders, under vacuum into a special quartz cell (0.1 cm path length) for DRS measurements. The experiments were performed under vacuum using “break-seal” technique. The DRS spectra were recorded on UV-2501 PC Shimadzu spectrometer with IRS-250A diffusion reflection attachment in the 190–900 nm range with a resolution of 2 nm. The DRS spectra are presented according to the Kubelka–Munk function [24]:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

where *R* is reflection coefficient.

2.5. DRIFTS studies

Samples of catalysts were placed, in form of dry powders, into a special cell for DRIFT measurements. The DRIFT spectra were recorded on a Shimadzu FTIR-8300 spectrometer with a DRS-8000 diffusion reflection attachment in the 400–6000 cm⁻¹ range with a resolution of 4 cm⁻¹ and are presented in form of the Kubelka–Munk function (1).

2.6. Polymerization

The catalysts were tested in ethylene slurry polymerization in a steel autoclave (1.0 and 0.2 l) under the following conditions: catalyst loading 0.05–0.15 g, heptane, temperature 80 °C, ethylene pressure 6 and 10 bar, co-catalyst Al(*i*-Bu)₃, polymerization for 1 h.

3. Results and discussion

3.1. Me₂SiInd₂ZrMe₂/MAO/SiO₂ catalysts

In the UV/vis spectrum of the catalyst Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂, presented in Fig. 1, an intensive absorption band is observed at 456 nm, while no absorption is detected in the region 600–800 nm, assigned to the d–d transition of Zr(III) indicating that no reduction of zirconocene complex occurs upon interaction with MAO/SiO₂.

In line with related observations in homogeneous solutions [21], the longest-wavelength absorption is shifted from its position at 387 nm for Me₂Si(Ind)₂ZrMe₂ changes from 387 to 456 nm after adsorption on the MAO/SiO₂ support, indicating the formation of species of type (C) under these conditions.

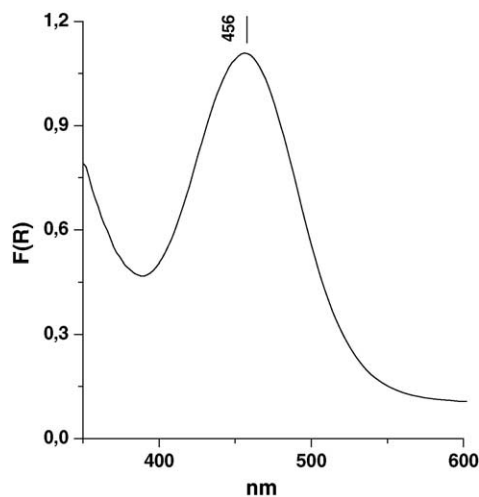


Fig. 1. UV/vis spectra of catalyst Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ (0.1 wt.% of Zr, Al_{MAO}/Zr = 514).

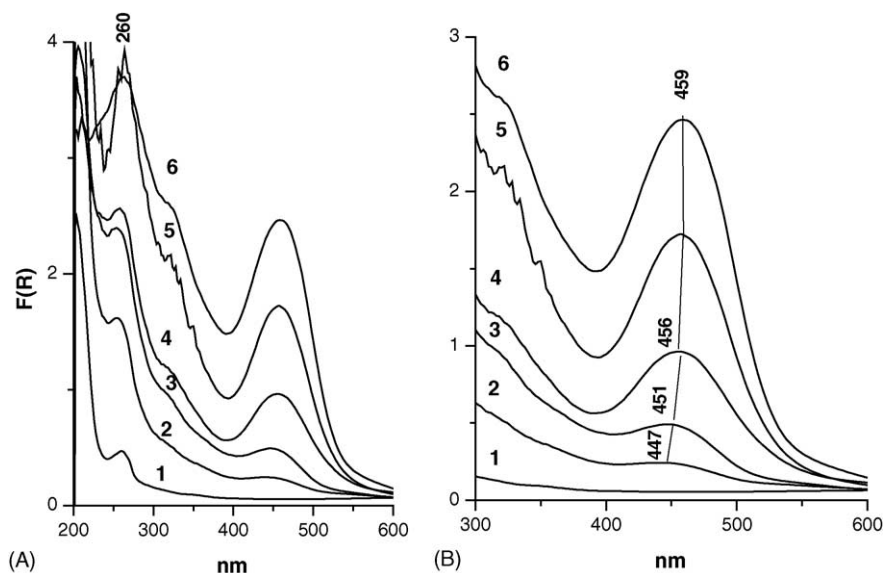


Fig. 2. UV/vis spectra of support MAO/SiO₂ (1) and catalysts Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ with different zirconium content, (2) 0.02% Zr (Al/Zr = 2550), (3) 0.05% Zr (Al/Zr = 1000), (4) 0.1% Zr (Al/Zr = 514), (5) 0.2% Zr (Al/Zr = 255) and (6) 0.5% Zr (Al/Zr = 100).

3.2. Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ catalysts

UV/vis spectra of MAO/SiO₂ support and of Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ catalysts with different zirconium contents are presented in Fig. 2.

UV/vis spectra of the MAO/SiO₂ support (Fig. 2) show only an absorption band at 260 nm of very low intensity. As observed for toluene solutions of Me₂Si(Ind)₂ZrCl₂, only one ligand to metal charge transfer (LMCT) absorption is observed in the 350–600 nm region in the spectra of the Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ catalysts.

For Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ catalysts with Zr contents of 0.2–0.5 wt.% (Al_{MAO}/Zr = 100–250) the longest-wavelength LMCT absorption is observed at 459 nm, but its position decreases to 447 nm upon decreasing the Zr content to 0.02 wt.% (Al_{MAO}/Zr = 2500).

The close similarity of the absorption at 459 nm with that observed at 456 nm for catalyst Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ and with the corresponding reaction system in homogeneous solutions strongly suggests that species of the type (C) are also formed in the catalyst system Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂.

Whether the shift of this absorption to somewhat lower wavelengths at decreased Zr contents is due the appearance of additional complex species or rather to consumption of minor complex amounts by surface impurities needs to be further clarified.

3.3. Activation of Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ and Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ catalysts with TIBA

Frequently, some AlR₃ compounds (TIBA or further MAO solution) is added to polymerization systems containing

supported zirconocene/MAO/SiO₂ catalysts. Therefore, we have further studied the catalyst systems Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ and Me₂Si(Ind)₂ZrCl₂/MAO/SiO₂ (0.1 wt.% of Zr, Al_{MAO}/Zr = 514) with regard to their activation by addition of TIBA at different Al_{TIBA}/Zr ratios.

UV/vis spectra of the Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ catalyst treated with TIBA at Al_{TIBA}/Zr = 60 and 400 (Fig. 3, spectra 2 and 3), are more complex than the initial spectrum of Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ catalyst. The position of the longest-wavelength LMCT band of the zirconocene is shifted by treatment with TIBA from 456 to 496 nm. The absorption at 496 nm can be assigned, according to the literature data in Table 1, to a hetero-bimetallic complex of type

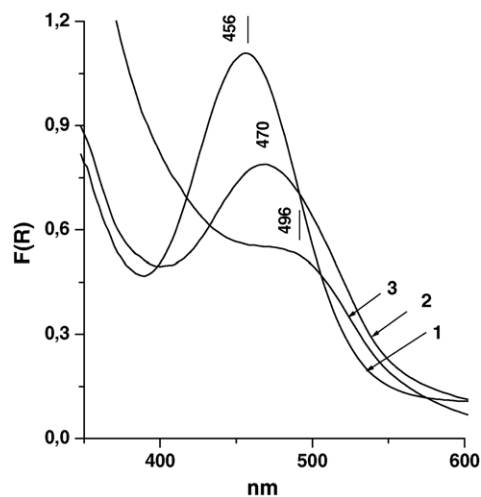


Fig. 3. UV/vis spectra of catalysts (1) Me₂Si(Ind)₂ZrMe₂/MAO/SiO₂ (0.1 wt.% of Zr, Al_{MAO}/Zr = 514), (2) catalyst (1) treated with TIBA at Al_{TIBA}/Zr = 60 and (3) catalyst (1) treated with TIBA at Al_{TIBA}/Zr = 400.

Table 1

UV/vis data for $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2$ ($\text{X} = \text{CH}_3, \text{Cl}$) complexes and cationic intermediates formed at interaction of zirconocene with MAO and borate activators [21]

	Complex	[Al]/[Zr] (mol/mol)	Position of LMCT (nm)
1	$\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$	–	446
2	$\text{Me}_2\text{SiInd}_2\text{ZrCl}(\text{Me})$	20	409
3	$\text{Me}_2\text{SiInd}_2\text{ZrMe}_2$	–	387
4	$[\text{Me}_2\text{SiInd}_2\text{ZrMe}]^+[\text{Me-MAO}]^-$ (C)	120	456
5	$[\text{Me}_2\text{SiInd}_2\text{Zr}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]^+[\text{Me-MAO}]^-$ (D)	2500	496
6	$[\text{Me}_2\text{SiInd}_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	–	560
7	$[\text{Me}_2\text{SiInd}_2\text{Zr}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$	–	488

(D). It should be noted that the intensity at 496 nm (Fig. 4, spectrum 3) is much lower than the intensity at 456 nm (Fig. 4, spectrum 1). This means that only a minor part of the surface zirconium species is transformed into structure (D) upon interaction with TIBA.

UV/vis spectra of $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst treated with TIBA are represented in Fig. 4. The band at 456 nm decreases in intensity and is slightly shifted to 451 nm after treatment of the $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst with TIBA at an Al/Zr ratio of 10 (Fig. 4, spectra 1 and 2). Treatment with TIBA at an Al/Zr ratio of 100, however, causes the band at 456 nm to disappear while two bands appear at 430 and 496 nm (Fig. 4, spectra 1 and 3). As in the case of $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ after treatment with TIBA, the intensity of these bands is lower, however, than that of the band at 456 nm in the initial catalyst.

Additional data on the surface zirconium species formed at interaction of catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ with

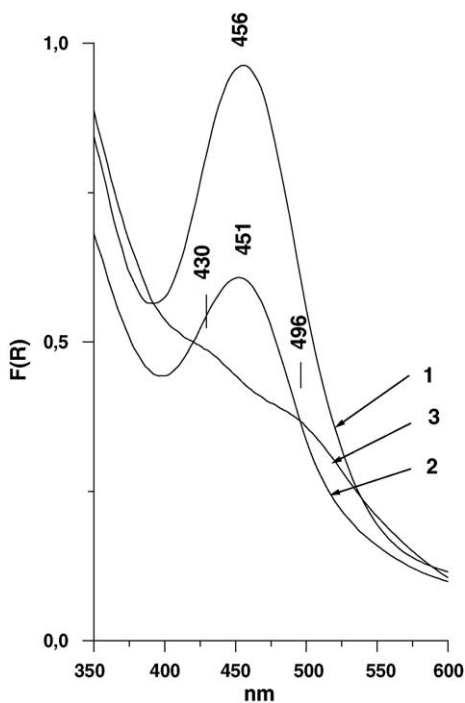


Fig. 4. UV/vis spectra (1) $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ (0.1 wt% Zr), (2) sample (1) treated with TIBA at Al/Zr = 10 and (3) sample (1) treated with TIBA at Al/Zr = 100.

TIBA have been obtained by means of DRIFTS (CO adsorption). CO insertion reaction into Zr–alkyl bond with formation of Zr–acyl derivatives is a well known reaction for different zirconium organic compounds [25–27]. So this reaction could serve as a probe on the formation of the reactive Zr–alkyl bonds in the surface zirconium species for the supported catalysts with different compositions.

The DRIFT spectrum of CO adsorbed on $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ is presented in Fig. 5 (spectrum 1). Adsorption of CO at 20 °C on the catalyst causes new a.b. within the range 1400–1600 cm^{-1} .

The DRIFT spectrum of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst treated with CO is presented in Fig. 5 (spectrum 2). Adsorption of CO at 20 °C on the catalyst causes new a.b. within the range 1400–1600 cm^{-1} too and additional a.b. at 1645 and 1665 cm^{-1} . The intensity of these a.b. in spectrum of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst is lower than one in the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ catalyst. These a.b. characterize acyl– (ν_{CO} 1600–1700 cm^{-1}) and η -acyl– (ν_{CO} 1525–1550 cm^{-1}) complexes of zirconium [25–27].

So according to these data initial $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst likewise to the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ contains the reactive zirconium–alkyl

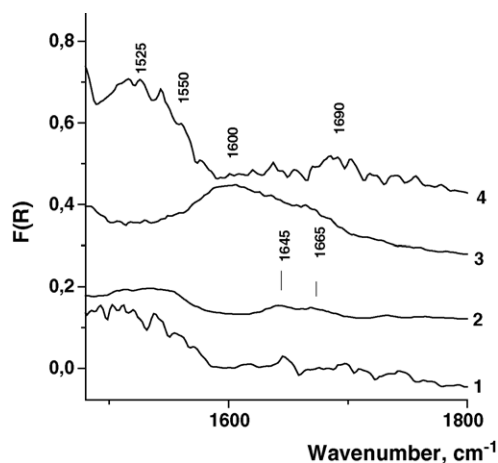


Fig. 5. Difference DRIFT spectra of adsorbed CO (0.45 atm) at 20 °C (1) $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ (0.1 wt.% of Zr, $\text{Al}_{\text{MAO}}/\text{Zr} = 514$), (2) $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ (0.1 wt.% of Zr, $\text{Al}_{\text{MAO}}/\text{Zr} = 514$), (3) TIBA/ $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ ($\text{Al}_{\text{TIBA}}:\text{Zr} = 10$) and (4) TIBA/ $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ ($\text{Al}_{\text{TIBA}}:\text{Zr} = 100$).

bonds. But the amount of these species in the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst is lower than one in the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ catalyst.

DRIFT spectra of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst treated with TIBA at different $\text{Al}_{\text{TIBA}}/\text{Zr}$ ratios and then CO are presented in Fig. 5 (spectra 1 and 2). A broad a.b. with two maximums at 1600 and 1665 cm^{-1} appears after treatment of the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst with TIBA at $\text{Al}_{\text{TIBA}}/\text{Zr} = 10$ and then with CO (Fig. 5, spectrum 3). a.b. at 1525, 1550 and 1690 cm^{-1} appear after treatment of the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ catalyst with TIBA at $\text{Al}_{\text{TIBA}}/\text{Zr} = 100$ and then with CO (Fig. 5, spectrum 4). Intensity of a.b. at 1500–1700 cm^{-1} region in the spectrum of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ treated with TIBA is higher than one of initial catalyst. The positions of these a.b. depends on the $\text{Al}_{\text{TIBA}}/\text{Zr}$ ratio. So according these data the most part of alkylated zirconium species is formed in the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ only after treatment with TIBA and $\text{Al}_{\text{TIBA}}/\text{Zr}$ ratio influences the alkylation extent and composition and structure of formed cationic species.

4. Polymerization

Additional data on the reactivity of the surface zirconium species in catalysts $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ ($\text{X}=\text{Cl}, \text{Me}$) have been obtained by means of DRIFTS (ethylene adsorption). The DRIFT spectra of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ ($\text{X}=\text{Me}, \text{Cl}$) treated with ethylene are presented in Fig. 6. New a.b. at 2920,

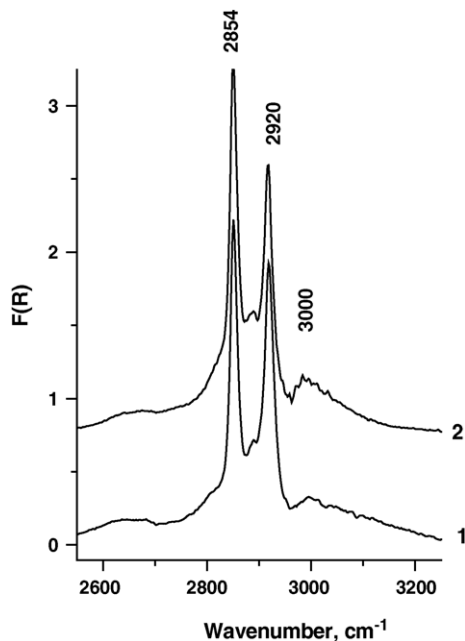


Fig. 6. Difference DRIFT spectra of (1) $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ (0.1 wt.% of Zr, $\text{Al}_{\text{MAO}}/\text{Zr} = 514$) and (2) $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ (0.02 wt.% of Zr, $\text{Al}_{\text{MAO}}/\text{Zr} = 2550$) treated with ethylene (40 tor) at 20 °C for 10 min and then vacuumated for 30 min at 20 °C.

Table 2

Data on the effect of TIBA on the activity of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ ($\text{X}=\text{Cl}, \text{Me}$) catalysts

Experiment	X	$\frac{\text{Al}_{\text{TIBA}}}{\text{Zr}}$	Activity, $\frac{\text{kg PE}}{\text{g Zr h bar}}$
1	Me	0	3.1
2	Me	500	10.5
3	Cl	0	0.3
4	Cl	70	6.5
5	Cl	320	7.9
6	Cl	515	9.4

(Experiments 1 and 2: $\text{X}=\text{Me}$: 0.1 wt.% of Zr, 9.6 wt.% of Al), (experiments 3–6: $\text{X}=\text{Cl}$: 0.08 wt.% of Zr, 6.25 wt.% of Al), polymerization in heptane at 80 °C, for 1 h, runs 1 and 2: ethylene pressure 10 bar, runs 3–6: ethylene pressure 6 bar.

2854 cm^{-1} appear after adsorption of ethylene on the $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ catalyst (Fig. 6). According to ref. [29] a.b. at 2920 and 2854 cm^{-1} characterize the stretching vibration of $-\text{CH}_2-$ group (ν_s and ν_{as}). So these data evidence polymerization proceeds at interaction of the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ with ethylene at 20 °C. These data are in agreement with the DRIFTS results presented in Fig. 5 (CO adsorption) that the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ contain the species of type (C) with reactive zirconium–alkyl bonds.

Comparative data on activity of these catalysts $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$ in ethylene polymerization are presented in Table 2. Activity of the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$ is very low while the activity of the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ is much higher (Table 2). Addition of TIBA proceeds to the great enhance of the activity for both catalysts. This effect is the more pronounced for the catalyst $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$. There are two possible reason of low activity of initial catalysts $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrX}_2/\text{MAO}/\text{SiO}_2$:

- (i) low concentration of the active species of the type (C);
- (ii) low reactivity of the active species of type (C) in comparison with the reactivity of the active species of type (D).

5. Conclusions

Based on the results presented above, it appears clear that the interaction of $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ with a MAO/SiO₂ support occurs in close analogy to the corresponding reaction systems in homogeneous solutions and gives primarily species of the type (C). To which degree these species are capable to induce the catalytic polymerization of olefins will depend on the nature and, in particular, the coordination strength of the anions X-MAO^- which are in contact with their Zr centers. This question will have to be investigated by direct activity measurements and spectroscopic data. Nevertheless, the absence of noticeable formation of species of type (D) under these conditions can be regarded as a first indication that the coordination of the X-MAO^-

anions present under the conditions of our study is too strong to allow their displacement by the (presumably low) AlMe_3 content of the samples and, hence, probably also too strong for substantial catalytic activity.

Further insights in this regard are derived from our studies on TIBA addition to these catalyst systems. TIBA is known to exchange Me groups available in a reaction system against *i*-Bu groups [28], since the availability of bridging Me ligands suitable for formation of mixed dimers of the type $i\text{Bu}_2\text{Al}(\mu\text{-Me})_2\text{Al}i\text{Bu}_2$ allows the electron-deficient tricoordinate Zr centers in bulky TIBA to acquire a more stable tetracoordinate geometry. The same is presumably true for exchangeable Cl^- ions, since the formation of mixed dimers of the type $i\text{Bu}_2\text{Al}(\mu\text{-Cl})_2\text{Al}i\text{Bu}_2$ is probably even more favorable. It appears quite likely, therefore, that addition of TIBA can transform, by exchange of Me and/or Cl units against *i*-Bu groups, the X-MAO⁻ anions, present in the species of type (C) initially formed in the catalyst systems $\text{Me}_2\text{SiInd}_2\text{ZrMe}_2/\text{MAO}/\text{SiO}_2$ and $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO}/\text{SiO}_2$, to some modified analogs of the type Y-MAO⁻, which are less strongly coordinating. The conversion of at least some fraction of species (C) to species of type (D) by TMA-induced displacement of the counter-anion, would indicate that these anions are less coordinating in the TIBA-treated than in the initial catalyst systems. If this indeed the case, the treatment with TIBA should also enhance the catalytic activities of these catalysts. Whether this is true, remains again to be tested experimentally in subsequent studies.

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