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An IR-Spectroscopic Study of the State of Zirconium in Supported Zirconocene Catalysts

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Abstract—The surface compounds of zirconium in $SiO_2/MAO/Cp_2ZrMe_2$ (**I**) and SiO_2/Cp_2ZrMe_2 (**II**) catalysts were studied by the IR spectroscopy of adsorbed CO at 93–293 K. It was found that the bridging and terminal complexes of CO were formed on the surface of the catalysts at 93 K; the adsorption of CO was reversible. At 293 K, CO was irreversibly inserted into the Zr–Me bond with the formation of various acyl compounds of zirconium; these compounds were characterized by absorption bands in the region 1495–1750 cm^{-1} in the IR spectrum. These data suggested the heterogeneity of the surface composition of zirconocene catalysts **I** and **II**. Catalyst **I**, which was active in ethylene polymerization, contained surface zirconium complexes that can be considered as the precursors of active centers for ethylene polymerization.

INTRODUCTION

Supported metallocene catalysts for olefin polymerization have been intensively studied in the past few years [1–9]. In the majority of relevant publications, the preparation of these catalysts, the kinetics of polymerization, and the properties of the resulting polymers were considered. Published physicochemical data on the formation of supported zirconocene catalysts and on the structure and composition of surface zirconium compounds are comparatively scarce.

With the use of ^{13}C CP MAS NMR spectrometry, Marks and coworkers [10–13] found that in the adsorption of metallocene compounds Cp'_2MR_2 ($Cp' = \eta^5$-$(CH_3)_5C_5$; M = Th, U, or Zr; R = alkyl) on Al_2O_3, SiO_2–Al_2O_3, $MgCl_2$, and ZrO_2/H_2SO_4 supports the alkyl group of the metallocene complex was transferred to the Lewis acid sites (LASs) of the support. As a result, a cation-like complex $[Cp'_2M]^+[R]^-$ immobilized on the surface of the support was formed. According to Marks and coworkers [10–13], these complexes are active in the reactions of olefin polymerization and hydrogenation. However, zirconocene catalysts based on these supports are much less active than silica modified with polymethylalumoxane (MAO) (SiO_2/MAO).

Previously [14], with the use of the IR spectroscopy of adsorbed CO, we found that two types of LASs occurred in the SiO_2/MAO and $SiO_2/Al(CH_3)_3$ systems: moderately strong ($\nu_{CO} = 2212$ cm^{-1}) and weak ($\nu_{CO} = 2192$ cm^{-1}) LASs. The Cp_2ZrMe_2 zirconocene reacted with all of the LASs of these supports; however, active centers were formed with the participation of only the strongest aprotic sites [15].

It is well known that carbon monoxide is convenient for the IR-spectroscopic studies of the coordination state and reactivity of alkyl and hydride zirconium compounds [16–20]. In particular, data on the coordination of CO to the hydride complexes of zirconium at 163 K followed by CO insertion into the Zr–R bond (R = H, alkyl) at 293 K with the formation of formyl and acyl complexes are known [16–18]. It was found [19, 20] that CO can react with cationic zirconium complexes to form σ-carbonyl complexes, for example, $[Cp_3Zr(CO)]^+[MeB(C_6F_5)_3]^-$ ($\nu_{CO} = 2150$ cm^{-1}).

In this work, we studied the interaction of CO with surface zirconium compounds in $SiO_2/MAO/Cp_2ZrMe_2$ and SiO_2/Cp_2ZrMe_2 catalysts with the use of IR spectroscopy.

EXPERIMENTAL

Davison 952 silica with a specific surface area of 260 m^2/g (0.04 wt % Al as an impurity) was used as a support, which was treated with a 0.2 M MAO solution in toluene (prepared by the dilution of a 1.8 M MAO solution from Witco (Berghamen)).

1. Sample Preparation for IR Spectroscopy

1.1. $SiO_2/MAO/Cp_2ZrMe_2$ (I). The silica was pressed as pellets with $\rho = 10$–25 mg/cm^2; the pellets were heated in air for 1 h at 773 K, rapidly transferred to a special cell for IR spectroscopy, and evacuated at 973 K (1 h) at a pressure of 2×10^{-2} Torr. Next, the cell was cooled to room temperature, and the sample was treated with a MAO solution in toluene (20 ml) for 0.5 h. Thereafter, the solution was decanted, and the pellet was washed three times with toluene, dried at 293 K to a residual pressure of 2×10^{-2} Torr, and treated with a solution of the zirconocene complex Cp_2ZrMe_2 (0.2 mmol per gram of the support) in hexane at 293 K for 20 min. Next, the solution was decant-

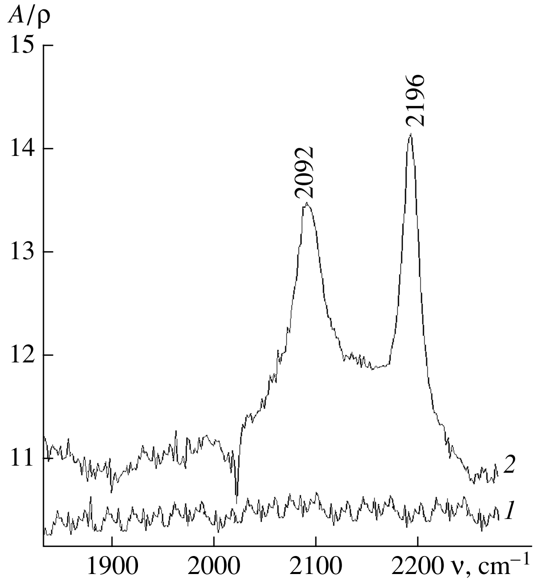


Fig. 1. IR spectra of (*1*) $SiO_2(973)/Cp_2ZrMe_2$ and (*2*) $SiO_2(973)/MAO/Cp_2ZrMe_2$ samples after the adsorption of C_2D_4 (80 Torr) at 298 K.

ed, and the pellet was washed three times with hexane and dried in a vacuum at 293 K (30 min) to a residual pressure of 1×10^{-2} Torr. The Al and Zr contents of the sample were 9.5 and 0.42 wt %, respectively (chemical analysis was performed using ICP AES [21]).

1.2. SiO_2/Cp_2ZrMe_2 (II). A silica pellet was heated in air at 773 K (1 h); next, it was placed in a cell for IR spectroscopy and evacuated (1 h) at 973 or 523 K ($SiO_2(973)$ or $SiO_2(523)$, respectively). The pellet was cooled and kept in 20 ml of a hexane solution of Cp_2ZrMe_2 (0.2 mmol per gram of the support) for 0.5 h. Then, the pellet was washed three times and dried at room temperature to a residual pressure of 10^{-2} Torr.

The Zr contents of the $SiO_2(973)/Cp_2ZrMe_2$ and $SiO_2(523)/Cp_2ZrMe_2$ samples were 1.48 and 2.73 wt %, respectively.

2. IR-Spectroscopic Procedure

CO was adsorbed at 93 and 293 K in portions from 0.1 to 10 Torr. The IR spectra were measured on an IFS-113V instrument (Bruker) with a resolution of 4 cm^{-1}. The results were presented as difference spectra obtained before and after CO adsorption.

The intensities of absorption bands in the IR spectra are given in absorbance units per gram of a catalyst in 1 cm^2 (A/g) or as A/ρ (the absorbance A of an absorption band ν normalized to the sample thickness).

In particular cases, absorption bands were deconvolved into individual Lorentzian components with the minimization of standard deviation.

RESULTS AND DISCUSSION

*1. Interaction of Catalysts **I** and **II** with Deuteroethylene*

After the adsorption of C_2D_4 at room temperature, the IR spectrum of the $SiO_2/MAO/Cp_2ZrMe_2$ catalyst exhibited two new absorption bands at 2092 and 2196 cm^{-1}, which characterize the CD stretching vibrations of the $-CD_2$-fragment of polydeuteroethylene (Fig. 1). However, the treatment of $SiO_2(523)/Cp_2ZrMe_2$ and $SiO_2(973)/Cp_2ZrMe_2$ samples and the parent SiO_2/MAO support with deuteroethylene did not cause changes in the spectra. As an example, Fig. 1 demonstrates the spectrum of C_2D_4 adsorbed on $SiO_2(973)/Cp_2ZrMe_2$. Thus, surface zirconium compounds with different reactivities toward ethylene were formed in the $SiO_2/MAO/Cp_2ZrMe_2$ and SiO_2/Cp_2ZrMe_2 systems.

With the use of ^{13}C CP MAS NMR spectrometry, it was found [10, 11] that two μ-oxo-like compounds, which are inactive in ethylene polymerization, were formed on the surface of SiO_2/Cp_2ZrMe_2 catalysts (Table 1, experiment no. 2).

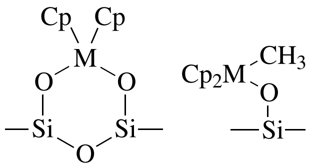
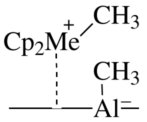
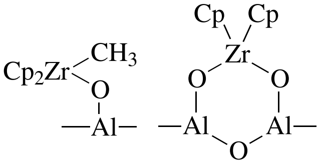
At the same time, in the interaction of zirconocene with the acid sites of MAO in $SiO_2/MAO/Cp_2ZrMe_2$ catalysts, cation-like zirconium complexes can be formed, which are typical of Cp_2ZrMe_2/MAO homogeneous systems [27–30]. However, the $SiO_2/MAO/Cp_2ZrMe_2$ supported catalysts are much less active than homogeneous analogs (Table 1). This is likely due to a lower number of active centers in supported catalysts. In this case, a considerable portion of surface zirconium compounds in the $SiO_2/MAO/Cp_2ZrMe_2$ catalyst can occur in the inactive form.

*2. Interaction of Catalysts **I** and **II** with CO at 93 K*

Absorption bands at 2136, 2155, 2170, and 2210 cm^{-1} appeared in the IR spectrum of parent $SiO_2(973)$ after CO adsorption (Fig. 2a, spectrum *1*). According to Panchenko *et al.* [14], an absorption band at 2136 cm^{-1} characterizes physically adsorbed CO, an absorption band at 2155 cm^{-1} characterizes a CO complex at the silanol groups of silica, an absorption band at 2170 cm^{-1} characterizes CO complexes at Brönsted acid sites (BASs), and an absorption band at 2210 cm^{-1} characterizes CO complexes at LASs. The occurrence of BASs and LASs on the surface of silica was related to the occurrence of a small amount of aluminum (0.04 wt %) as a constituent.

After the treatment of silica with a solution of Cp_2ZrMe_2, absorption bands at 2136, 2155, and 2170 cm^{-1} were retained, whereas an absorption band at 2210 cm^{-1} disappeared and new absorption bands appeared at 1890 and 2143 cm^{-1} (Fig. 2a, spectrum *2*; Fig. 2b). Note that the intensity of the absorption band at 2170 cm^{-1} decreased; this fact is indicative of the interaction of zirconocene molecules with BASs.

Table 1. Main zirconium compounds in homogeneous and supported metallocene systems and catalytic activity in ethylene polymerization

Experiment no.	Catalyst	Zirconium compounds	Activity, (kg PE) (g Zr)$^{-1}$ h^{-1} atm^{-1}*
1	Cp_2ZrMe_2/MAO	$[Cp_2ZrMe]^+[Me\text{-}MAO]^-$ [28–30]	700
2	$SiO_2(973)/Cp_2ZrMe_2$	 [10, 11]	Trace PE
3	$SiO_2/MAO/Cp_2ZrMe_2$	 [14, 15]	12.4
4	$Al_2O_3(773)/Cp_2ZrMe_2$	 [10, 11]	0.01

Note: Polymerization in heptane for 1 h at 353 K and an ethylene pressure of 10 atm; cocatalyst, Al(*iso*-C_4H_9)$_3$. Results of this work (experiment nos. 2–4).

* Polymerization in toluene for 1 h at 343 K and an ethylene pressure of 8 atm; [Al]/[Zr] = 50000; Zr = 10^{-7} mol [31] (experiment no. 1).

The appearance of a broad absorption band at 1890 cm^{-1} in the IR spectrum after the adsorption of CO suggests the formation of Zr(CO)Zr or Zr(CO)Al bridging groups. Analogous complexes (absorption bands at 1897–1870 cm^{-1}) were observed in the low-temperature adsorption of CO on Zr–Rh/SiO_2 and Zr–Rh/Al_2O_3 catalysts [24].

Previously [15], we found that the treatment of a SiO_2/MAO sample with zirconocene resulted in the interaction of Cp_2ZrMe_2 with the LASs of the support. Because of this, the corresponding absorption bands disappeared. Evidently, the disappearance of an absorption band at 2210 cm^{-1} from the IR spectrum of the $SiO_2(973)/Cp_2ZrMe_2$ sample was due to analogous interactions.

The absorption band at 2143 cm^{-1} can characterize the complex of CO with cation-like zirconium compounds; however, more accurate attribution of this absorption band will be given below.

The spectrum of CO adsorbed on the SiO_2/MAO support (Fig. 3a, spectrum *1*) consists of several absorption bands: 2212, 2192, 2160, 2136, and 1880 cm^{-1}. According to published data [14, 24], absorption bands at 2212 and 2192 cm^{-1} characterize the LASs of the SiO_2/MAO sample, an absorption band at 2160 cm^{-1} characterizes hydrogen-bonded OH groups, and an absorption band at 1880 cm^{-1} characterizes Al(CO)Al bridging groups.

After the adsorption of CO on the surface of $SiO_2/MAO/Cp_2ZrMe_2$, absorption bands at 2212 and 2192 cm^{-1} disappeared from the IR spectrum, and new absorption bands appeared at 2036, 2124, and 2146 cm^{-1} (Fig. 3a, spectrum *2* and Fig. 3b). The absorption band intensity at 1880 cm^{-1} dramatically decreased, and a shift to the high-frequency region was observed (ν = 1895 cm^{-1}). A decrease in the intensity of this band suggests the interaction of zirconocene with the SiO_2/MAO support; this interaction resulted in the formation of a smaller amount of Al(CO)Al bridging groups on the surface after CO adsorption. The high-frequency shift of this absorption band can be explained by the fact that aluminum or zirconium compounds with a higher charge, as compared with the SiO_2/MAO support, were formed on the surface.

The disappearance of absorption bands at 2212 and 2192 cm^{-1} from the IR spectrum of CO adsorbed on $SiO_2/MAO/Cp_2ZrMe_2$ provides support for our previous conclusion [15] on the interaction of zirconocene with the LASs of the SiO_2/MAO support.

It is well known that at 183 K CO can coordinate to homogeneous organozirconium complexes, in particular, the hydrides of Zr^{4+} in the $[(C_5Me_5)_2Zr(H)_2CO]$ system (ν(CO) = 2044 cm^{-1} [16, 17]) and the surface hydrides of Zr^{4+} in $SiO_2/Zr(BH_4)_4$/250°C (ν(CO) = 2040 cm^{-1} [17, 18]). On the contrary, $(C_5Me_5)_2Zr(Me_2)$ at temperatures to 87 K does not form coordination complexes with CO [16, 17]. According to these data, it is believed that an absorption band at 2036 cm^{-1} in the

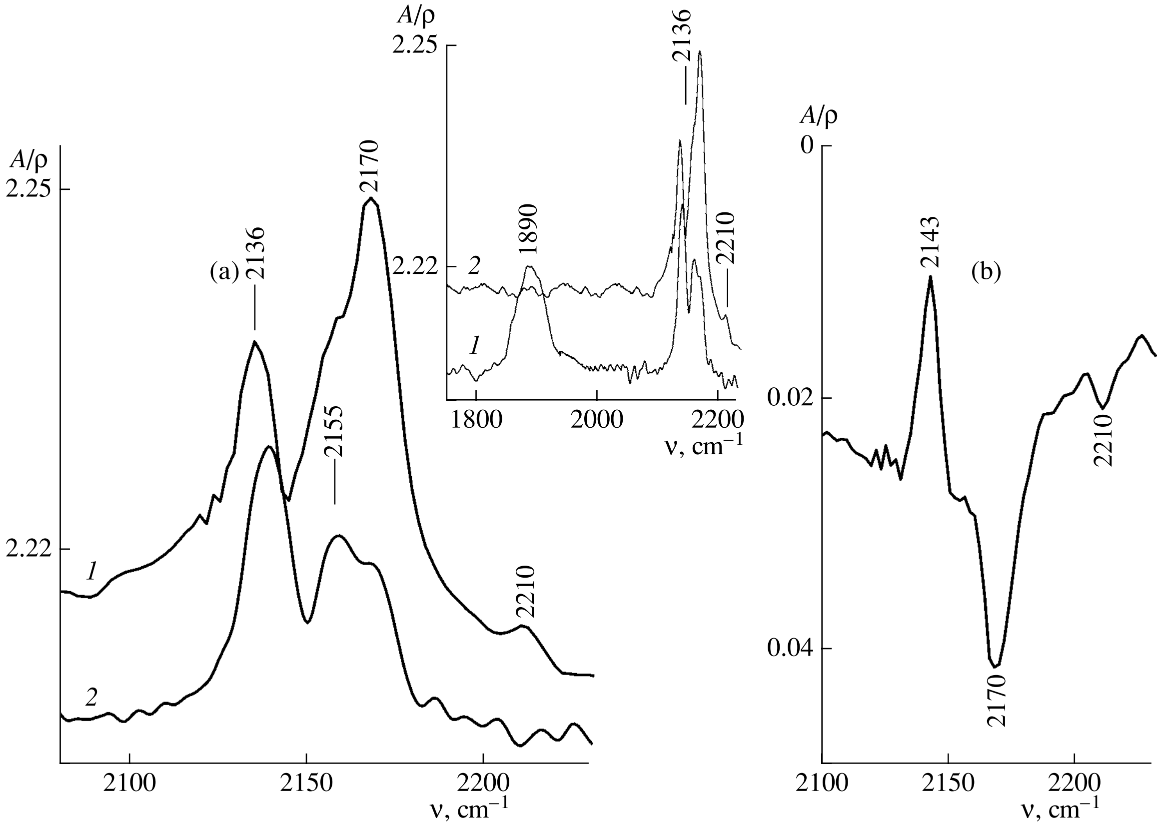


Fig. 2. (a) IR spectra of CO (0.1 Torr) adsorbed on (*1*) SiO_2(973) and (*2*) $SiO_2(973)/Cp_2ZrMe_2$ (1.45 wt % Zr) samples at 93 K and (b) the difference spectrum obtained by the subtraction of the IR spectrum of the SiO_2(973) sample from the spectrum of the $SiO_2(973)/Cp_2ZrMe_2$ sample.

spectrum of the $SiO_2/MAO/Cp_2ZrMe_2$ system characterizes CO coordinated terminally to the surface hydride compounds of zirconium. Note that the formation of zirconium hydride compounds in the $(C_5H_4R)_2ZrCl_2/MAO$ (where R = H, *tert*-Bu, or Me_3Si) and $CpZrCl_3/MAO$ homogeneous systems was suggested previously [22, 23].

It is well known [25] that changes in the oxidation state and coordination of a cation strongly affect the position of the absorption band of adsorbed CO. Table 2 summarizes the frequencies of the stretching vibrations of carbonyl groups in the homogeneous carbonyl complexes of zirconocenes of various composition. It can be seen that the carbonyl complexes of Zr(II) are characterized by low values of ν(CO). In the case of a cation-like carbonyl complex (Table 2, entry 5), nonclassical σ-carbonyl complexes of zirconium were formed. In this case, the absorption bands of linear carbonyl groups were shifted toward higher frequencies

Table 2. Stretching vibration frequencies of carbonyl groups in zirconocene complexes

No.	Compound	Oxidation state of Zr	ν(CO), cm⁻¹	*T*, K	References
1	$Cp_2Zr(CO)PPh_3$	II	1857	293	[16]
2	$Cp_2Zr(CO)_2$	II	1883, 1973	293	[16]
3	$Cp_2ZrMe_2^*$	IV	–	293, 163	[16]
4	$[(C_5Me_5)_2Zr(H)_2 \longleftarrow CO]$	IV	2044	163	[16, 17]
5	$[Cp_3Zr(CO)]^+[MeB(C_6F_5)_3]^-$	IV	2150	273	[19, 20]
6	$[Cp_2ZrMe \longleftarrow (CO)]^{\delta+}[Me–MAO]^{\delta-}/SiO_2$	IV	2123, 2146	93	This work

* Does not adsorb CO.

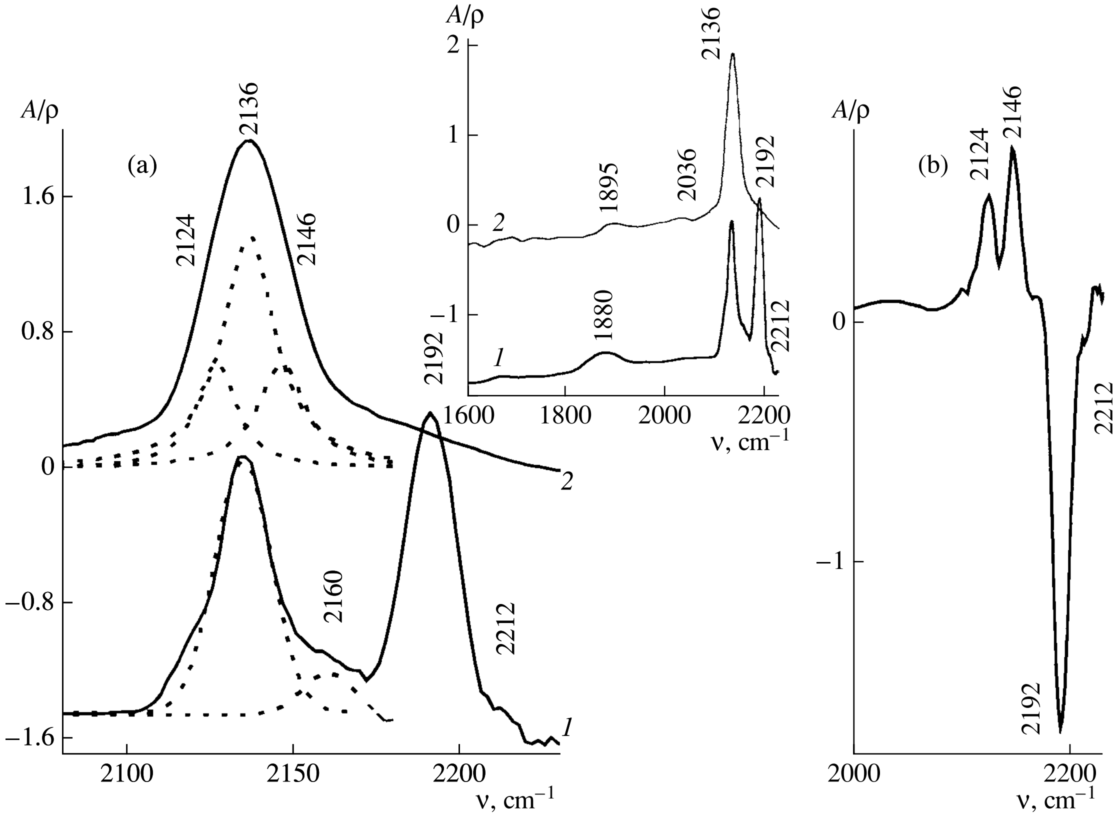


Fig. 3. (a) IR spectra of CO (0.1 Torr) adsorbed on (*1*) SiO_2(973)/MAO and (*2*) SiO_2(973)/MAO/Cp_2ZrMe_2 (0.42 wt % Zr) samples at 93 K and (b) the difference spectrum obtained by the subtraction of the IR spectrum of the SiO_2(973)/MAO sample from the spectrum of the SiO_2(973)/MAO/Cp_2ZrMe_2 sample.

(ν(CO) = 2150 cm^{-1}) [19, 20], as compared with a neutral complex (Table 2, entry 4).

Based on these data, we assumed that absorption bands in the region 2120–2150 cm^{-1} can correspond to the cation-like complexes of zirconium formed on the surface of SiO_2/MAO/Cp_2ZrMe_2 or SiO_2(973)/Cp_2ZrMe_2. It is likely that the absorption bands at 2124, 2143, and 2146 cm^{-1} in the IR spectra of SiO_2(973)/Cp_2ZrMe_2 and SiO_2/MAO/Cp_2ZrMe_2 samples characterize CO coordinated to the zirconium ion in cation-like complexes bearing different charges (Figs. 2b, 3b). However, these bands have low intensities against the background of physically adsorbed CO (ν = 2136 cm^{-1}); therefore, they appeared only in a difference spectrum (Figs. 2, 3). The above absorption bands were also detected by resolving a band contour at 2136 cm^{-1} into individual components.

Thus, the occurrence of three absorption bands at 2036, 2124, and 2146 cm^{-1} in the IR spectrum of SiO_2/MAO/Cp_2ZrMe_2 is indicative of the presence of various types of surface zirconium compounds in this sample.

It is well known [18] that the adsorption of CO on surface organozirconium compounds at $T \leq 163$ K is reversible. Indeed, the evacuation of the SiO_2/MAO/Cp_2ZrMe_2 sample after CO adsorption at 93 K resulted in the disappearance of absorption bands at 1895, 2036, 2124, 2136, and 2146 cm^{-1}, which appeared again after repeatedly adding CO (Fig. 3, spectrum *2*).

Thus, according to data obtained using the IR spectroscopy of adsorbed CO, the SiO_2/MAO/Cp_2ZrMe_2 catalyst, which is active in ethylene polymerization, contains several types of surface zirconium compounds. In this case, two zirconium complexes (absorption bands at 2124 and 2146 cm^{-1}) can be assigned to cation-like structures.

*3. Interaction of Catalysts **I** and **II** with CO at Room Temperature*

According to published data [16–18], an increase in the temperature of CO adsorption resulted in the insertion of carbon monoxide molecules into the Zr–R bond and in the formation of η^2-acyl and formyl compounds of zirconium, which are characterized by absorption bands with ν(CO) = 1525–1540 cm^{-1} in the IR spectra.

Figure 4 demonstrates the IR spectra of the SiO_2/MAO/Cp_2ZrMe_2 sample treated with CO at 93 K and then heated to 203 and 293 K. As the temperature

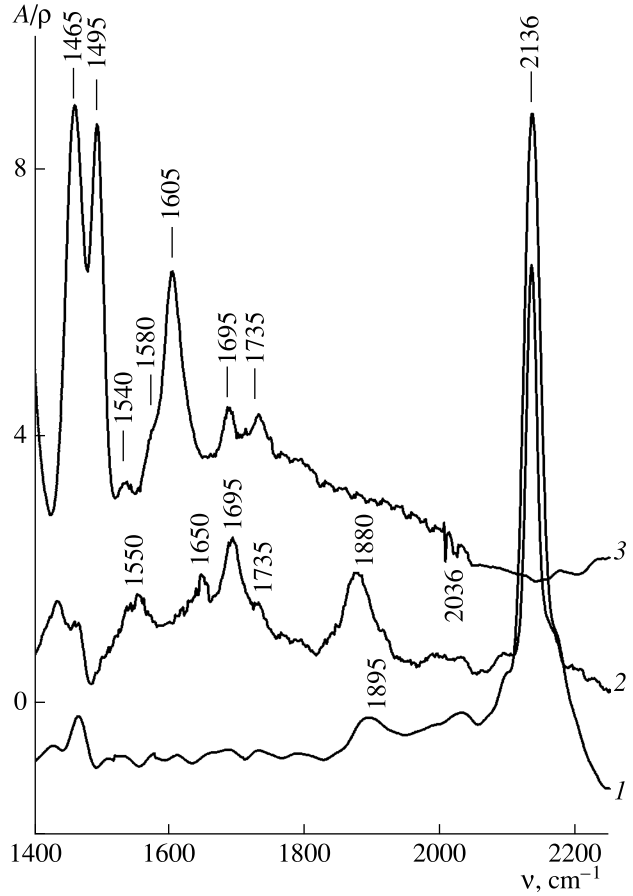


Fig. 4. IR spectra of CO (0.2 Torr) adsorbed on the SiO_2(973)/MAO/Cp_2ZrMe_2 (0.42 wt % Zr) sample at (*1*) 93, (*2*) 203, and (*3*) 293 K.

was increased to 203 K, new absorption bands with ν(CO) = 1550, 1650, 1695, and 1753 cm^{-1} appeared in the spectrum; an absorption band at 1895 cm^{-1} shifted to the low-frequency region (1880 cm^{-1}), and the intensities of absorption bands at 2136 and 2036 cm^{-1} decreased (Fig. 4, spectrum *2*). After increasing the temperature of CO adsorption to 293 K, absorption bands at 1465, 1495, 1540, 1580, 1605, 1695, and 1735 cm^{-1} appeared in the spectrum, whereas absorption bands at 2036 and 2136 cm^{-1} disappeared (Fig. 4, spectrum *3*). According to Sverdlov *et al.* [26], the absorption band at 1465 cm^{-1} can be attributed to the C–H deformation vibrations of CH_3 groups. The bands with ν(CO) = 1495, 1540, 1580, 1605, 1695, and 1735 cm^{-1} can characterize the η^2-acyl compounds of zirconium [16–18], which may be formed by the insertion of CO molecules into Zr–CH_3 bonds in surface zirconium compounds. The absorption bands at 1495, 1540, 1580, 1605, 1695, and 1735 cm^{-1} did not disappear after sample evacuation at 293 K. Thus, the insertion of CO molecules is irreversible.

Based on the experimental data, we concluded that several surface zirconium compounds containing methyl and hydride bonds were formed in the interaction of Cp_2ZrMe_2 with the SiO_2/MAO support. These compounds react with carbon monoxide to form acyl and formyl complexes of zirconium.

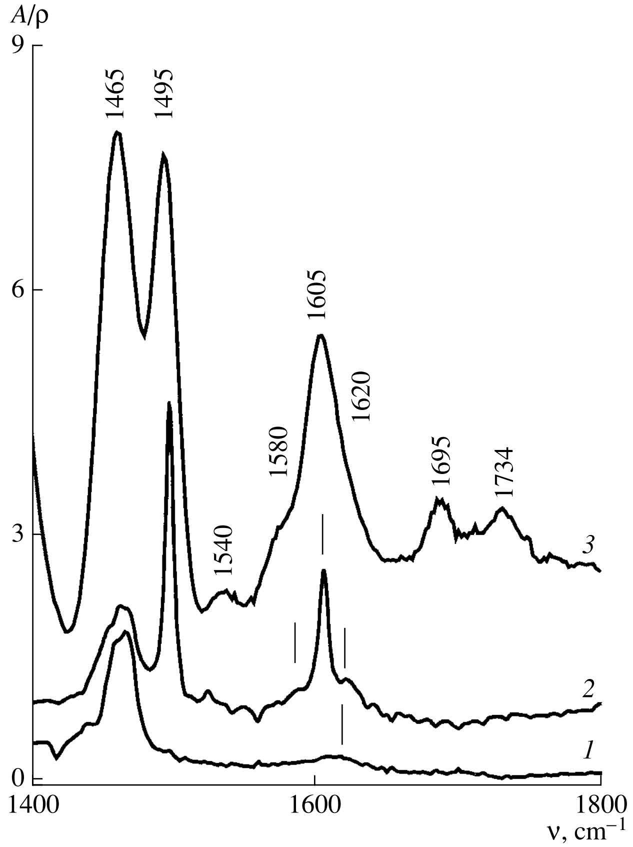


Fig. 5. IR spectra of CO adsorbed at 293 K on the following samples: (*1*) SiO_2(523)/Cp_2ZrMe_2, (*2*) SiO_2(973)/Cp_2ZrMe_2, and (*3*) SiO_2(973)/MAO/Cp_2ZrMe_2.

Figure 5 demonstrates the IR spectra of the SiO_2(523)/Cp_2ZrMe_2, SiO_2(973)/Cp_2ZrMe_2, and SiO_2/MAO/Cp_2ZrMe_2 systems after CO adsorption at 293 K. As mentioned above, the first two systems are inactive in ethylene polymerization.

The spectrum of the SiO_2(523)/Cp_2ZrMe_2/CO sample does not contain absorption bands in the region 1500–1750 cm^{-1}, which are characteristic of the acyl compounds of zirconium. Evidently, this is due to the fact that zirconium compounds with no Zr–Me bonds primarily occurred at the surface of this catalyst.

The IR spectrum of the SiO_2(973)/Cp_2ZrMe_2/CO sample exhibited absorption bands at 1495, 1540, 1580, and 1605 cm^{-1}, which correspond to the acyl compounds of zirconium. Analogous absorption bands were also present in the spectrum of the SiO_2/MAO/Cp_2ZrMe_2 sample. In addition to these bands, the spectrum contained two absorption bands at 1695 and 1735 cm^{-1}, which belonged to the acyl compounds of zirconium. Thus, at least six various methyl and hydride compounds of zirconium were detected in the SiO_2/MAO/Cp_2ZrMe_2 catalyst. These compounds react with CO to form the corresponding acyl and formyl complexes of zirconium (1495, 1540, 1580, 1605, 1695, and 1734 cm^{-1}). In this case, the first four complexes (1495, 1540, 1580, and 1605 cm^{-1}), which were also detected in the SiO_2(923)/Cp_2ZrMe_2 catalyst, belong to zirconium compounds that are inactive in ethylene polymerization. Only zirconium compounds that form acyl complexes, characterized by absorption bands at 1695 and 1735 cm^{-1}, by the interaction with CO and occur only in the SiO_2(923)/Cp_2ZrMe_2 catalyst can be considered as the precursors of active centers. It is likely that the amount of these zirconium compounds is small, and the majority of surface zirconium compounds belongs to inactive states.

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