

IRS study of ethylene polymerization catalyst SiO₂/methylaluminoxane/zirconocene

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Abstract

IR spectroscopy has been used to study the interaction of silica with two methylaluminoxane (MAO) samples differed by trimethylaluminium (TMA) content and with TMA. MAO and TMA have been shown to react with silica in a different way. Whereas TMA interacts with terminal hydroxyl groups of silica via the protolysis reaction, MAO mainly adsorbs on the surface hydroxyl groups of silica without noticeable protolytical reaction with them. When silica is treated with commercial grade MAO with significant TMA content, the silica surface hydroxyl groups mainly interacts with TMA and MAO adsorbs on the surface of SiO₂/TMA sample. Lewis acidic sites (LAS) of silica, modified with TMA and MAO samples differed by TMA content, have been investigated by IR spectroscopy (CO adsorption as probe molecule at 77 K). Two types of LAS were found on the surface of silica modified with MAO and TMA: LAS of moderate strength ($\nu_{\text{CO}} = 2204\text{--}2212\text{ cm}^{-1}$) and weak LAS ($\nu_{\text{CO}} = 2194\text{ cm}^{-1}$). The concentration of these acidic sites was estimated. By anchoring of Cp₂ZrCl₂ on silica, modified with TMA and MAO, the corresponding catalysts SiO₂/TMA/Cp₂ZrCl₂ and SiO₂/MAO/Cp₂ZrCl₂ were prepared and tested at ethylene polymerization. Some correlations between the amount and strength of surface LAS of supports, catalysts composition and their activity are discussed. It is proposed that the surface active species are formed at zirconocene interaction with the most strong LAS. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: IR spectroscopy; Methylaluminoxane; Trimethylaluminium; Silica supported catalyst; Lewis acidic sites; Ethylene polymerization; Supported metallocene catalysts

1. Introduction

The catalysts for olefin polymerization derived from metallocene compounds and methylaluminoxane (MAO) have been intensively investigated in the last years. The point of extreme interest is the developing of supported catalysts with metallocene compound as the active component [1–10]. It is assumed, that the active species of metallocene based catalysts are cationic complex of the type

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$[\text{Cp}_2\text{M-R}]^+$ (M = Th, Zr), formed due to the interaction of metallocene compound with the Lewis acidic sites of the support (Al_2O_3 , MgCl_2) [11].

Direct application of silica as a support for metallocene catalysts preparation resulted in inactive catalysts formation [1–4]. The general method for silica supported metallocene catalysts preparation is based on the utilization of silica, treated with alkylaluminium compounds and, particularly, with MAO. On further anchoring of metallocene compound supported polymerization catalysts can be prepared.

Few data are known about MAO interaction with silica. In Ref. [12] it was shown by IR spectroscopy that terminal hydroxyl groups of silica disappear after silica treatment with MAO. But we should keep in mind that MAO is a complex substance and it consists of oligomeric MAO molecules with composition $[-\text{Al}(\text{CH}_3)\text{O}-]_n$ ($n = 6-30$) and the significant amount of highly reactive trimethylaluminium (TMA) [13–15]. So the actual role of MAO in the reaction with silica remains unclear.

It is possible to propose that MAO adsorbed on silica contains the Lewis acidic sites responsible for the following interaction with metallocene compound, but no data on the reactive sites of MAO adsorbed on silica are known.

In the present work we have used IR spectroscopy to study the interaction of silica support with TMA and with two MAO samples, containing TMA in various amounts.

IR spectroscopy of adsorbed carbon monoxide as probe molecule was used to get data on the Lewis acidic sites (LAS) of silica, modified with MAO. The characterization of the LAS for alumina, zeolites and etc. using IR spectroscopy of adsorbed probe molecules, in particular, carbon monoxide, is widely used now [16–21]. CO is one of the most suitable surface probe, because in the adsorbed state its stretching frequency is highly sensitive to local fields (at positively charged sites), to hydrogen bonding, and to σ -bond formation on sites with Lewis acid character. Low temperature CO adsorption is the effective method of LAS investigation due to the small value of CO adsorption heat (30–70 kJ/mol). Furthermore there is the very low probability for any side-reactions causing rearrangement of the support reactive centres under low temperature CO adsorption. So in the present work we have used low temperature CO adsorption (77 K) for Lewis acidic sites of SiO_2/MAO supports characterization.

2. Experimental

Silica Davison 952 (surface area $260 \text{ m}^2/\text{g}$) has been used as support. This silica contains 0.04% wt. of alumina as admixture.

Methylaluminoxane was purchased from Witco (Berghamen) as toluene solution (total Al content 1.8 M, Al as $\text{Al}(\text{CH}_3)_3$ 0.5 M).

MAO-1: the sample of commercial MAO (as toluene solution with concentration of Al_{total} 1.8 M) was used as purchased.

MAO-2 (MAO with reduced amount of AlMe_3): the sample of MAO-1 was distilled under vacuum. The obtained solid product with concentration of $\text{Al}_{\text{total}} = 38.5 \text{ wt.}\%$ (polymer MAO with residual AlMe_3) was dissolved in purified toluene to obtain the solution with concentration of Al_{total} 0.1 M, concentration of Al as TMA is 0.003 M.

AlMe_3 solution: according to ^1H NMR data, the liquid fraction, separated at MAO-1 distillation, contains only AlMe_3 . The measured amount of this fraction was diluted with toluene to prepare 0.5 M solution.

2.1. Preparation of samples for IRS studies

The silica powder was pressed in tablets (mass typically 20–40 mg, $\rho = 9\text{--}15\text{ mg/cm}^2$). The silica tablet was heated at 400°C for 1 h in air, then it was placed in a special cell, allowing heating of the support tablet in vacuum and its treatment with MAO or TMA solutions. The silica tablet was heated at 400°C for 1 h under vacuum (10^{-2} Torr) and then cooled to the ambient temperature. The IR spectrum of the dehydrated sample was recorded for reference purposes. Then the silica tablet treated by 20 ml of MAO or TMA solution for 0.5 h. The support tablet was washed three times with toluene and dried, at 40°C for 1 h under vacuum to residual pressure of 10^{-2} Torr.

IR spectra were registered with IFS-113 V Bruker spectrometer, resolution being 2 cm^{-1} .

LAS are identified by adsorption bands for adsorbed CO in region higher than 2180 cm^{-1} . In order to identify LAS of different strengths, CO was adsorbed in small doses (0.02 Torr) up to CO pressure 5 Torr at 77 K.

LAS content was calculated according to Ref. [17] from the expression

$$A = 10^{-3} \cdot A_0 \cdot C_s \cdot \rho \quad (1)$$

where A is the apparent integral absorption of the examined band (cm^{-1}); A_0 —the apparent integral adsorption coefficient for CO adsorbate concentration $1\text{ }\mu\text{mol/g}$, ($\text{cm}/\mu\text{mol}$), C_s —the concentration of acidic centres ($\mu\text{mol/g}$); ρ —amount of the sample per 1 cm^2 beam, (g/cm^2).

The concentration of LAS was determined from the intensity of the observed peaks under the conditions of saturation with adsorbate, at 77 K using a coefficient of integral adsorption A_0 equal 1.1, 1.0 and $0.95\text{ cm}/\mu\text{mol}$ for LAS at 2212 and 2210, 2204 and 2194 cm^{-1} respectively [18].

IR spectra are given in relative units $\text{Absorbance}/\rho$, that means that optical density (A_ν) at wavenumber (ν) is normalised to tablet thickness ρ . For example, if the value of optical density (A_ν) consists 0.05 for tablet with $\rho = 10\text{ mg/cm}^2$, the value of $\text{Absorbance}/\rho$ will be 5. IR spectra in the ν_{CO} region are presented as difference spectra of the sample before and after CO adsorption.

2.2. Preparation of support samples

The measured sample of silica was heated at 400°C for 3 h in air and for 3 h under vacuum, then it was treated by MAO or TMA solution ($[\text{Al}]/[\text{Si-OH}] = 10$). Thus obtained suspension was stirred at 20°C for 0.5 h. Reaction products and residual aluminium compounds were washed out by toluene (three times). The modified supports were dried at room temperature under vacuum.

2.3. Catalysts preparation

The solution of Cp_2ZrCl_2 in toluene (0.2 mmol Zr/g of support) was added to toluene suspension of measured support sample. The resulting suspension was stirred at 20°C for 30 min. Then the liquid fraction was decanted, the solid part was washed up three times with toluene and dried in vacuum at room temperature.

Catalysts with the reduced Zr content were prepared by support treatment with measured amount of Cp_2ZrCl_2 solution to provide the desired Zr content. Catalyst was dried in vacuum without washings.

2.4. Support and catalyst composition

The content of Al and Zr in the samples were determined by atomic-emission spectrometry-inductively coupled plasma (AES-ICP) [22].

2.5. Ethylene polymerization

Polymerization of ethylene was performed in a steel autoclave (0.2 L). During the polymerization ethylene pressure and temperature were maintained constant. The conditions used for polymerization are given in Table 4.

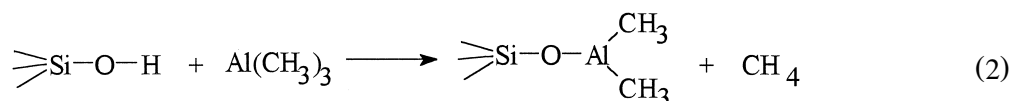
3. Results and discussion

3.1. IRS study of silica interaction with TMA and MAO

MAO is the product of TMA partial hydrolysis and includes the oligomeric molecules of MAO $(\text{MeAlO})_n$ and, usually, the significant amount of TMA associated with MAO [13–15]. When silica is treated with MAO, its surface OH-groups are able to interact with both MAO components—oligomers $(\text{MeAlO})_n$ and TMA. To clarify the mode of MAO components to interact with silica hydroxyl groups, the samples prepared by silica treatment with TMA and with MAO, containing different amount of TMA (MAO-1 and MAO-2) have been investigated. Data on the aluminium content in the samples prepared and corresponding molar ratio between the amount of Al anchored with silica and content of OH-groups in the initial silica are given in Table 1.

Fig. 1 shows the IR spectra of initial silica (curve 1) and that of the TMA treated silica (SiO_2/TMA , curve 2) and MAO treated silica ($\text{SiO}_2/\text{MAO-1}$, curve 3; $\text{SiO}_2/\text{MAO-2}$, curve 4). On TMA reaction with silica at room temperature, the band at 3745 cm^{-1} of silica terminal hydroxyl groups (Si–OH) disappears completely. The intensity of 3680 cm^{-1} band, corresponding to hydrogen-bonded OH-groups, changes insignificantly. Besides this, two intensive bands at 2944 and 2894 cm^{-1} and two low intensity bands at 2850 and 2830 cm^{-1} , characterising the stretching vibrations of (CH_3) -groups, appear in the IR spectrum of SiO_2/TMA sample.

The results obtained corresponds to the data of Refs. [23–26]. According to Refs. [23,24] TMA reacts with silica terminal OH-groups via protolysis reaction (2) yielding methane.



This resulted in terminal OH-groups band at 3745 cm^{-1} disappearance (Fig. 1, curve 1 and 2).

Table 1

Data on the aluminum content in the tablet of silica^a treated by different aluminiumorganic compounds (AOC)

Run no.	AOC	[Al]		[Al]/[OH] ^a (mol)
		% wt.	$\mu\text{mol/g}$	
1	AlMe_3	3.85	1420	1.6
2	MAO-1	10.30	3815	4.3
3	MAO-2	1.45	537	0.6

^aOH-groups content in the initial silica (SiO_2 400) is $880\text{ }\mu\text{mol/g}$ [27].

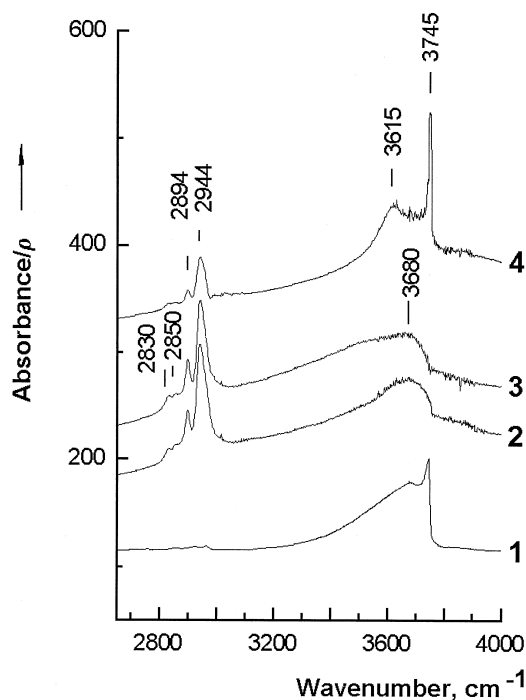
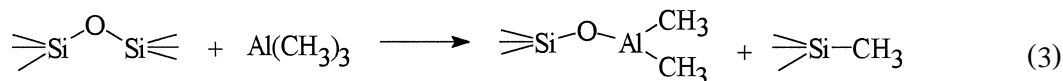


Fig. 1. IRS data for SiO₂ modified with AOC: (1) initial SiO₂ (*T_d* = 400°C); (2) SiO₂ + AlMe₃; (3) SiO₂ + MAO-1; (4) SiO₂ + MAO-2.

According to Ref. [25], TMA is able to interaction with silica siloxane groups via the reactions (3):



Surface compounds Si-CH₃ and additional amount of surface alkylaluminium compounds are formed due to this reaction. Basing on the data of Ref. [25], the bands at 2944, 2894, 2850 and 2830 cm⁻¹ (Fig. 1, curve 2) can be attributed to the stretching vibrations of methyl groups in (Al-CH₃)-fragments of surface alkylaluminium compounds and in (Si-CH₃) species. Unfortunately, since the stretching vibrations of methyl groups in (Al-CH₃)- and (Si-CH₃)-fragments are very similar, they are not distinguished by IR spectroscopy.

Our chemical analysis data (Table 1) proves the occurrence of reaction (3) on TMA interaction with the silica surface: the Al content in SiO₂/TMA sample was found to be higher than that of OH-groups in the initial silica ([Al]/[OH] = 1.6) (Table 1, run 1).

The IR spectrum of the sample, prepared by silica treatment with commercial grade MAO (SiO₂/MAO-1) is shown in Fig. 1 (curve 3). It is similar to the IR spectra of SiO₂/TMA sample (Fig. 1, curve 2).

The amount of Al in the (SiO₂/MAO-1) sample (10.3% wt., [Al]/[OH] = 4.3, Table 1, run 2) significantly exceeds that in the sample SiO₂/TMA (Table 1, run 1).

It may be assumed, that when MAO with high content of TMA is used for silica treatment, the most part of silica terminal OH-groups interacts particularly with TMA, but some amount of oligomeric MAO molecules strongly adsorb on SiO₂/TMA surface.

In the sample prepared using MAO with diminished amount of TMA ($\text{SiO}_2/\text{MAO-2}$) the content of strongly fixed Al is significantly lower than that in SiO_2/TMA and $\text{SiO}_2/\text{MAO-1}$ samples (Table 1, run 3). For $\text{SiO}_2/\text{MAO-2}$ sample the molar ratio $[\text{Al}]/[\text{OH}] = 0.6$. So a significant portion of silica hydroxyl groups does not react with MAO-2. The IRS data prove this conclusion (Fig. 1, curve 4). Indeed, for this sample the intensity of 3745 cm^{-1} band (terminal OH-groups) decreases insignificantly (approximately by $1/4$).

The spectrum of $\text{SiO}_2/\text{MAO-2}$ sample contains a new band at 3615 cm^{-1} not observed in the spectra of SiO_2/TMA and $\text{SiO}_2/\text{MAO-1}$. Possibly, the band at 3615 cm^{-1} can be attributed to silica terminal OH-groups, bound by hydrogen bonds with oxygen atoms or methyl groups of adsorbed MAO oligomeric molecules. It is known [17,18,21] that hydrogen bonds formation shifts the position of the band, characterising silica terminal OH-groups to the low field direction. In our case it can be shifted from 3745 to 3615 cm^{-1} .

To get more details about MAO and TMA interaction with silica surface, we studied the low temperature (77 K) CO adsorption on the samples prepared.

Fig. 2 shows the IR difference spectra before and after CO adsorption on SiO_2 , SiO_2/TMA , $\text{SiO}_2/\text{MAO-1}$ and $\text{SiO}_2/\text{MAO-2}$ samples.

Two bands are observed in the spectrum of silica (Fig. 2, curve 1): the intensive band at 3654 cm^{-1} and 3486 cm^{-1} band. According to Refs. [18,21] the band at 3654 cm^{-1} can be ascribed to the terminal OH-groups of silica with CO adsorbed.

According to Refs. [18,19,21], CO adsorption on more acidic bridging OH-groups in $\text{Si}-(\text{OH})-\text{Al}$ fragments is characterised by high value of $\Delta\nu_{\text{OH}}$ ($\Delta\nu_{\text{OH}} = 250\text{--}300 \text{ cm}^{-1}$). Possibly, the band at 3486 cm^{-1} in SiO_2 spectrum can be attributed to this type of OH-groups, because the observed value of $\Delta\nu_{\text{OH}}$ is 259 cm^{-1} (from 3745 cm^{-1} to 3486 cm^{-1}). The groups $\text{Si}-(\text{OH})-\text{Al}$ may initially exist in the silica due to the admixture of aluminium (0.04% wt.). The possible amount of $\text{Si}-(\text{OH})-\text{Al}$

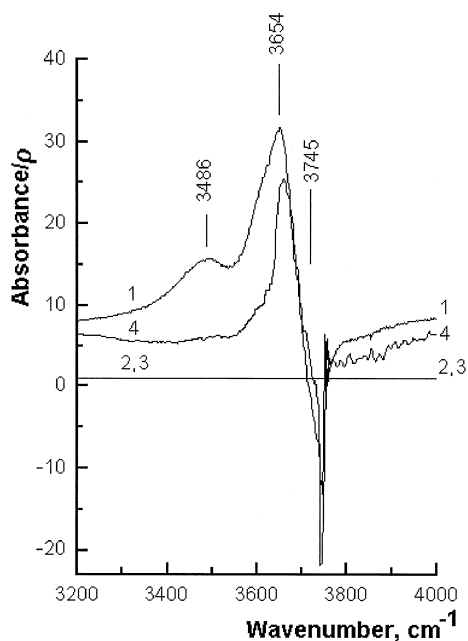


Fig. 2. Difference IR spectra of CO adsorbed at 77 K (0.18 Torr). (1) Initial SiO_2 ($T_d = 400^\circ\text{C}$); (2) $\text{SiO}_2 + \text{TMA}$; (3) $\text{SiO}_2 + \text{MAO-1}$; (4) $\text{SiO}_2 + \text{MAO-2}$.

fragments, calculated from analytical data ($15 \mu\text{mol/g}$ of SiO_2), corresponds to the amount of these groups ($20 \mu\text{mol/g}$ of SiO_2), evaluated from our IR data according to Refs. [17,18].

No changes within the range $3200\text{--}4000 \text{ cm}^{-1}$ were detected in the spectra of SiO_2/TMA and $\text{SiO}_2/\text{MAO-1}$ samples after CO adsorption (Fig. 2, curves 2, 3). This result corresponds to the absence of the terminal OH-groups in these samples (Fig. 1, curves 2, 3).

The spectrum of $\text{SiO}_2/\text{MAO-2}$ sample (Fig. 2, curve 4) exhibited the only band at 3654 cm^{-1} due to adsorption of CO on to silica terminal OH-groups, whereas 3486 cm^{-1} band of bridging (Si-(OH)-Al) was not detected. Probably, in contrast to silica terminal OH-groups, its more acidic (Si-(OH)-Al) groups are able to react with MAO oligomers via protolysis reaction.

3.2. IRS study of the Lewis acidic sites in the silica modified with MAO and TMA

We have used IR spectroscopy of CO adsorbed at low temperature for characterization of LAS in the silica modified with MAO (SiO_2/MAO) and silica modified with TMA (SiO_2/TMA).

As it was noted above silica sample used contains 0.04 wt.% of aluminium. It was shown above too, that due to the presence of aluminium the groups Si-(OH)-Al are formed. Hydroxyl groups of this type are stronger Brønsted acids in comparison with ordinary Si-OH groups of silica.

The aluminium admixture can promote the origin of some LAS in initial silica sample (the initial LAS). To distinguish this LAS from the centers, appeared due to silica modification with MAO and TMA, we investigated firstly the initial silica. The experiments with low temperature CO adsorption on silica, dehydroxylated at 700°C (SiO_2 700) and 400°C (SiO_2 400) have been done. IR spectra of adsorbed CO on (SiO_2 700) and (SiO_2 400) samples are shown in Fig. 3 (curve 1 and 2 correspondingly). The bands at 2138 , 2158 , 2175 , 2210 cm^{-1} are observed in the spectrum of (SiO_2 700) sample (curve 1). The 2138 cm^{-1} band can be attributed to the physically adsorbed CO species [18,20,21]. The band at 2158 cm^{-1} characterize CO species weakly bound up to silica OH-groups. The band at 2175 cm^{-1} can be attributed to CO complexes with Brønsted acidic centers (probably Si-(OH)-Al groups). The 2210 cm^{-1} band characterize surface LAS of moderate strength [18,20,21]. The concentration of this LAS in (SiO_2 700) sample, calculated is given in Table 3.

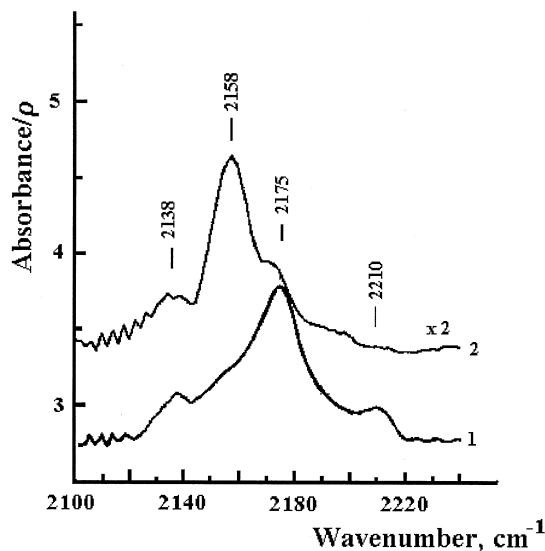


Fig. 3. Difference IR spectra of CO adsorbed at 77 K (0.18 Torr). (1) SiO_2 ($T_d = 700^\circ\text{C}$); (2) SiO_2 ($T_d = 400^\circ\text{C}$).

IR spectrum of CO adsorbed on (SiO_2 400) sample (Fig. 3.2) exhibits the same bands as (SiO_2 700) sample with the only difference that the band at 2210 cm^{-1} was absent. So initial LAS observe in the silica dehydroxylated at high temperature (700°C); initial LAS are absent in silica, dehydroxylated at 400°C . Therefore we have used the silica (SiO_2 400) as the support for further work.

IR spectra of CO adsorbed on the samples of silica, modified with TMA, MAO-1 and MAO-2 are shown on Fig. 4. The observed maxima for CO absorption spectra are summarized in Table 2. The spectra of all samples contain the band at 2138 cm^{-1} of physically adsorbed CO species and the bands in the region $2190\text{--}2220 \text{ cm}^{-1}$, corresponding to LAS with different strength [16,17,20,21]. In the spectrum of CO on SiO_2/TMA sample the bands (ν_{CO}) at 2194 and 2204 cm^{-1} (Fig. 4.1) were observed, the spectrum of $\text{SiO}_2/\text{MAO-1}$ sample contains the bands at 2194 and 2212 cm^{-1} (Fig. 4.2). The spectrum of CO on the sample $\text{SiO}_2/\text{MAO-2}$ is more complicated (Figs. 3.3 and 4.3) As in the previous cases, the band of physically adsorbed CO (ν_{CO} 2138 cm^{-1}) and the bands of surface LAS (ν_{CO} 2194 and 2212 cm^{-1}) are presented. Besides this, the spectrum contains the band at 2158 cm^{-1} corresponding to CO complexes with OH-groups of silica.

According to data of Refs. [18,21], four types of surface LAS can be identified in aluminium oxides by IR spectroscopy of adsorbed CO: strong LAS (S LAS) are characterized by the bands in the region $2235\text{--}2225 \text{ cm}^{-1}$, LAS of moderate strength (M LAS) with the bands in $2215\text{--}2203 \text{ cm}^{-1}$ region, and two types of weak LAS (W LAS) with the characteristic bands at $2200\text{--}2185 \text{ cm}^{-1}$ and $2182\text{--}2178 \text{ cm}^{-1}$. By analogy with this assumption, the bands in the region $2212\text{--}2204 \text{ cm}^{-1}$ of SiO_2/TMA and SiO_2/MAO samples can be attributed to surface M LAS, and the band at 2194 cm^{-1} to W LAS (Table 2).

From the spectra presented in Fig. 4 we have calculated the concentration of LAS in SiO_2/TMA and SiO_2/MAO samples. The results are summarized in Table 3.

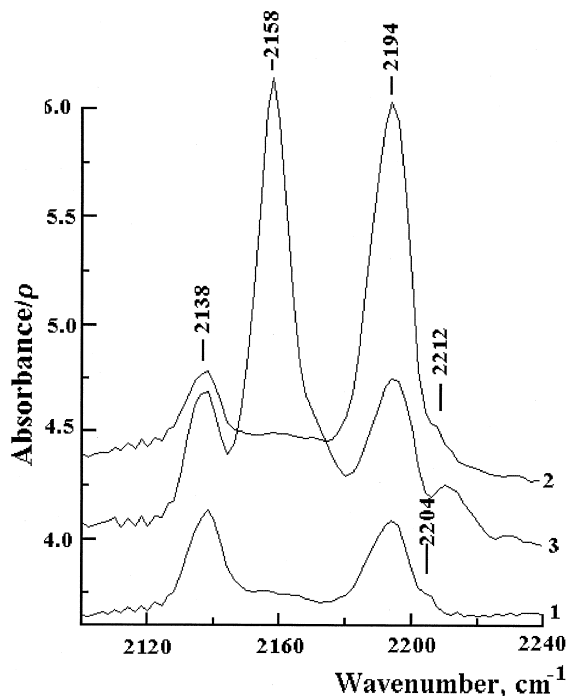


Fig. 4. Difference IR spectra of CO adsorbed at 77 K (0.18 Torr). (1) SiO_2/TMA ; (2) $\text{SiO}_2/\text{MAO-1}$; (3) $\text{SiO}_2/\text{MAO-2}$.

Table 2
IR band position for CO, adsorbed on acid sites of SiO₂/MAO(TMA) samples

Run no.	Sample	Lewis acid sites, ν_{CO} in cm^{-1}	
		M LAS	W LAS
1	SiO ₂ /TMA	2204	2194
2	SiO ₂ /MAO-1	2212	2194
3	SiO ₂ /MAO-2	2212	2194

Data of Table 3 show, that the highest total content of LAS was found for silica, treated with MAO-1, this correlate with the highest Al content in this sample (Table 2, Run 3). The content of LAS in SiO₂/MAO-2 sample (Table 2, Run 4) is only twice lower than that in SiO₂/MAO-1 sample, whereas the Al content is seven times lower.

The ratio between the content of M LAS and W LAS in the investigated samples is different. The minimal content both of M LAS and W LAS was found for SiO₂/TMA sample (Table 2, Run 2). The highest content of M LAS was estimated for the sample SiO₂/MAO-2 (Table 2, Run 4), SiO₂/MAO-1 sample contained mainly W LAS (Table 2, Run 3). The data presented in Table 3 on the ratio Al_{total}/LAS show, that in SiO₂/MAO-2 sample the number of surface aluminium atoms exhibiting Lewis acidity is higher than that in SiO₂/MAO-1. So, due to the interaction of silica surface OH-groups with TMA mainly W LAS are formed, whereas the stronger surface LAS originate from adsorbed oligomeric MAO species (SiO₂/MAO-2). But it should be noted, that MAO-2 is fixed on silica surface via adsorption and the most part of silica OH-groups remains unreacted.

It may be assumed, that three-coordinated aluminium atoms with different ligand environment act as Lewis acidic sites of the investigated supports, but there is not enough experimental data to discuss the structure of this sites in details.

3.3. Supported zirconocene catalysts based on SiO₂/TMA(MAO). The composition and catalytic properties in ethylene polymerization

Using MAO and TMA modified silica samples as supports, the catalysts containing Cp₂ZrCl₂ as active component have been prepared. Data on composition and catalytic activity in ethylene polymerization of the supported catalysts are given in Table 4.

Comparison of data on aluminium content in the supports and corresponding catalysts (Table 4), prepared using the excess of metallocene compound and several washings, show that TMA and MAO-2 are strongly bound up with silica, whereas aluminium compound from SiO₂/MAO-1 support is partly desorbed in the course of catalyst preparation (Table 4, runs 1, 2, 5).

Table 3
LAS content in SiO₂/TMA and SiO₂/MAO samples

Run	Sample	Al content		LAS content ($\mu\text{mol/g}$)			Al total/ LAS total	Al total/ M LAS
		% wt.	$\mu\text{mol/g}$	Total	M LAS	W LAS		
1	SiO ₂ (700)	0.04	15	1.0	1.0	–	15	15
2	SiO ₂ /TMA	3.9	1420	7.4	0.2	7.2	192	7100
3	SiO ₂ /MAO-1	10.3	3815	28.6	0.8	27.8	133	4770
4	SiO ₂ /MAO-2	1.45	537	15.8	2.7	13.1	34	199

Table 4
Data on composition and activity of catalysts SiO₂/TMA(MAO)/Cp₂ZrCl₂

Run	Support	Composition (μmol/g)			Activity ^a
		Support	Catalyst		
			Al	Al	
1	SiO ₂ /TMA	1333	1333	6.5	4.3
2	SiO ₂ /MAO-1	3815	2778	9.0	37.4
3 ^b	SiO ₂ /MAO-1	3815	3815	1.0	57.7
4 ^b	SiO ₂ /MAO-1	3815	3815	0.1	257
5	SiO ₂ /MAO-2	593	593	87.9	1.6
6 ^b	SiO ₂ /MAO-2	593	593	9.0	0

^aIn kg polyethylene per g Zr per h.

^bCatalysts prepared by adsorption of measured amount of Cp₂ZrCl₂.

Polymerization conditions: temperature 80°C, ethylene pressure 9 atm, in 70 ml of heptane, for 1 h, cocatalyst Al(*i*-Bu)₃, 25 μmol/ml.

As it was pointed out in the introduction, it is assumed, that Lewis acidic sites play the key role in the formation of the active species of metallocene-based supported catalysts [5]. So, we compared the data on the zirconium content and catalytic activity of the catalysts prepared with the data on the LAS evaluated above.

The amount of zirconocene anchored on the modified silica surface depends on the modifier used. Among the catalysts investigated, the catalyst SiO₂/TMA/Cp₂ZrCl₂ contains the minimal amount of Zr (6.5 μmol/g SiO₂, Table 4, run 1), and it is close to the total LAS content found for SiO₂/TMA support (7.4 μmol/g SiO₂, Table 2, run 2). Probably, in this case zirconocene compound is fixed on the surface via interaction both with W LAS and M LAS of the support.

The amount of strongly adsorbed zirconium in the catalyst prepared using SiO₂/MAO-1 as the support was slightly higher than that found for the catalyst SiO₂/TMA/Cp₂ZrCl₂, but its activity at ethylene polymerization was noticeably higher (Table 4, run 2). The amount of strongly adsorbed zirconium in this catalyst (9.0 μmol/g Table 3, run. 2) was noticeably higher than M LAS content (0.8 μmol/g, Table 3, run. 2) and lower than W LAS content (28 μmol/g, Table 3, run 2). The catalyst, prepared by adsorption of Cp₂ZrCl₂ taken in amount close to M LAS content (0.8 μmol/g, Table 2, run 3), exhibited the increase of activity (Table 4, run 3). On further decrease of the amount of zirconocene compound used for catalyst preparation, the activity of the system sharply increased (Table 4, run 4). Probably, when the support is treated with very small amount of Cp₂ZrCl₂, its interaction with the strongest LAS occurs first, leading to the maximal yield of active surface species.

The higher zirconium content was found for the catalyst SiO₂/MAO-2/Cp₂ZrCl₂ (Table 4, run 5). Its value (87.9 μmol/g) is considerably higher than LAS content found for the support SiO₂/MAO-2 (15.8 μmol/g, Table 3, run 4). This can be due to the interaction of zirconocene compound not only with surface LAS of this support, but with the residual silanol groups present in this support, as well (Fig. 1, curve 4, Table 2, run 3). The surface zirconium compounds formed via interaction with silanol groups are inactive at ethylene polymerization. Data of Table 4 show, that the activity of the catalyst SiO₂/MAO-2/Cp₂ZrCl₂ is lower than that of the catalysts prepared with SiO₂/TMA and SiO₂/MAO-1. Supporting of the reduced amount of Cp₂ZrCl₂ on SiO₂/MAO-2 resulted in the loss of catalyst activity (Table 4, run 6). Probably Cp₂ZrCl₂ interacts firstly with the residual silanol groups of the support SiO₂/MAO-2 with formation of the non-active zirconocene compounds.

Finally it is possible to conclude that zirconocene interacts with Lewis acidic sites of MAO at the formation of the catalyst SiO₂/MAO/zirconocene. Active species of this catalyst are formed at zirconocene interaction with the most strong LAS.

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