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IRS study of ethylene polymerization catalyst SiO_2/MAO/zirconocene

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Summary

Lewis acidic sites (LAS) of silica, modified with TMA and MAO samples differed by TMA content, have been characterized 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 : M LAS of moderate strength (ν_{CO} = 2204-2212 cm^{-1}) and weak W LAS (ν_{CO} = 2194 cm^{-1}). The concentration of these acidic sites has been estimated.

It was shown by IRS study CP_2ZrMe_2 interacts both with W LAS and M LAS. Correlation between the amount of M LAS and the activity of ethylene polymerization has been found.

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 a metallocene compound as the active component (1-10). The general method for silica supported metallocene catalysts preparation is based on the utilization of silica, treated with alkylaluminium compounds and, particularly, with MAO, for further metallocene compound adsorption.

It is possible to propose that MAO adsorbed on silica contains the Lewis acidic sites responsible for the following interaction with the metallocene compound, but data on the reactive sites of MAO adsorbed on silica are unknown.

We have used IR spectroscopy of adsorbed carbon monoxide as probe molecule for 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 (11-16).

Experimental

Silica Davison 952 (surface area 260 m^2/g) has been used as support.

MAO-1: The sample of commercial MAO (Witco) as toluene solution with a concentration of Al_{total} 1.8 M was used as purchased. This sample containes of 28% of Al_{total}, as $AlMe_3$ (by ^1H NMR data).

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MAO-2 (MAO with reduced amount of $AlMe_3$ (TMA)): The sample of MAO-1 was distilled under vacuum.. The obtained solid product (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 was 0.003 M.

For IRS studies the silica powder was pressed in tablets. The silica tablet was heated at 400°C for 1 h in air, then it was placed in a special cell, allowing to heat the support tablet in vacuum and its treatment with MAO or zirconocene solution.

IR spectra were registered with IFS-113V Bruker spectrometer.

CO was adsorbed in small doses (0.02 Torr) up to a CO pressure of 5 Torr at 77 K. The LAS content was calculated according to (12, 13, 15, 17)

IR spectra are given in relative units A/ρ, 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 ρ=10 mg/cm^2, the value of A/ρ will be 5.

IR spectra in the ν_{CO} region are presented as difference spectra of the sample before and after CO adsorption.

Ethylene polymerization was performed with catalyst prepared with SiO_2 powder as support using a procedure similar to the IRS study. Polymerization was carried out in a steel reactor (0.2 L) at 80°C in heptane.

Results and Discussion

Earlier we have studied the interaction of MAO and TMA with silica by IRS (17). According to data obtained in (17) when silica is treated with commercial grade MAO with significant TMA content (MAO-1), the silica surface hydroxyl groups mainly interact with TMA and MAO adsorbs on the surface of SiO_2/TMA sample. MAO purified of excess of TMA (MAO-2) mainly adsorbs on the surface hydroxyl groups of silica without noticeable protolytical reaction with them. The support SiO_2/MAO-2 contains a big amount of free hydroxyl group.

1. Characterization of surface Lewis acidic sites in $Si0_2$/MAO (TMA) supports by IRS of adsorbed CO

IR spectra of CO adsorbed on the samples of silica, modified with TMA, MAO-1 and MAO-2 are shown on Fig. 1 The spectra of all samples contain the band at 2138 cm^{-1} of physically adsorbed CO and the bands in the region 2190 - 2220 cm^{-1}, corresponding to LAS with different strength (11, 12, 15, 16). In the spectrum of CO on SiO_2/TMA sample the bands at 2194 and 2204 cm^{-1} were observed (Fig. 1.1), the spectrum of SiO_2/MAO-1 sample contains the bands at 2194 and 2212 cm^{-1} (Fig. 1.2). The spectrum of CO on the sample SiO_2/MAO-2 is more complicated (Fig. 1.3). As in the previous cases the bands of surface LAS (ν_{CO} 2194 and 2212 cm^{-1}) are presented. Additionally the spectrum contains the band at 2158 cm^{-1} corresponding to CO complexes with OH-groups of silica.

According to data of ref. (18, 13, 16), four types of surface LAS can be identified in aluminium oxides by IR spectroscopy of adsorbed CO: strong LAS are characterized by the bands in the region 2235-2225 cm^{-1}, LAS of moderate strength (M LAS) with the bands in the 2215-2203 cm^{-1} region, and two types of weak LAS (W LAS) with the characteristic bands at 2200-2185 cm^{-1} and 2182-2178 cm^{-1}. By analogy with this assumption, the bands in the region 2212-2204 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.

From the spectra presented in Fig. 1 we have calculated the concentration of LAS in SiO_2/TMA and SiO_2/ MAO samples. The results are summarized in Tab. 1.

The data of Tab. 1 show, that the highest total content of LAS was found for silica, treated with MAO-1. The content of LAS in SiO_2/MAO-2 sample is only half the size of the SiO_2/MAO-1 sample, whereas the Al content is seven times lower.

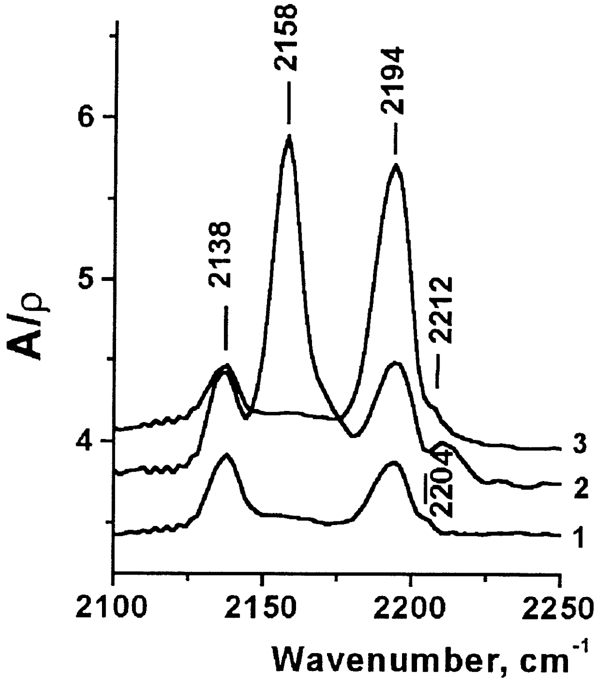

Fig. 1. Difference IR spectra of CO adsorbed at 77 K (0.18 Torr): 1 - SiO_2/TMA; 2- SiO_2/ MAO-1; 3 - SiO_2/MAO-2

Table 1. LAS content in SiO_2/ TMA and SiO_2/ MAO samples.

Run	Sample	Al content		LAS content, μmol/g			Al total/ LAS total	Al total/ M_{LAS}
		%wt.	μmol/g	Total	M_{LAS}	W_{LAS}		
1	SiO_2 / TMA	3.9	1420	7.4	0.2	7.2	192	7100
2	SiO_2 / MAO-1	10.3	3815	28.6	0.8	27.8	133	4770
3	SiO_2/ MAO-2	1.45	537	15.8	2.7	13.1	34	199

The smallest content both of M LAS and W LAS was found for the SiO_2/TMA sample. The highest content of M LAS was estimated for the sample SiO_2/MAO-2. The data presented in Tab. 1 on the ratio Al total/LAS show, that in the SiO_2/MAO-2 sample the number of surface aluminium atoms exhibiting Lewis acidity is higher than that in SiO_2/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 (SiO_2/MAO-2). But it should be noted, that MAO-2 is fixed on silica surface via adsorption and the biggest part of the silica OH-groups remains unreacted.

2. On the interaction of Cp_2ZrMe_2 with SiO_2/MAO support and connection of activity at ethylene polymerization with Lewis acidic sites of the support.

Two catalyst have been prepared by adsorption of Cp_2ZrMe_2 on the support SiO_2/MAO-1.

Catalyst A: the support was treated with the excess of a Cp_2ZrMe_2 solution at 20°C. The liquid fraction was decanted, the solid part was washed three times with toluene and dried in vacuum.

Catalyst B: the support was treated with a measured amount of a Cp_2ZrMe_2 solution to provide the desired zirconium content. Catalyst was dried in vacuum without washings.

The LAS of the initial supports and catalysts A and B have been characterized by IRS of adsorbed CO. IR spectra of CO adsorbed on the support and catalyst A are presented in Fig.2. Data of LAS content in the supports and catalyst A and B, zirconium content and activity at ethylene polymerization are presented in Tab.2. We can see the treatment of the support SiO_2/MAO-1 by excess of Cp_2ZrMe_2 (catalyst A), results to the disappearance of the bands at 2194 cm^{-1} and 2212 cm^{-1} (W LAS and M LAS respectively).

The data of the amount of zirconium anchored with the support SiO_2/MAO-1 are corresponded to the decreasing of the LAS amount after adsorbtion of Cp_2ZrMe_2 ($Zr/\Delta LAS \approx 1$, both for catalysts A and B, Tab.2). Activity of the catalyst B is much higher than one of catalyst A (Tab.2).

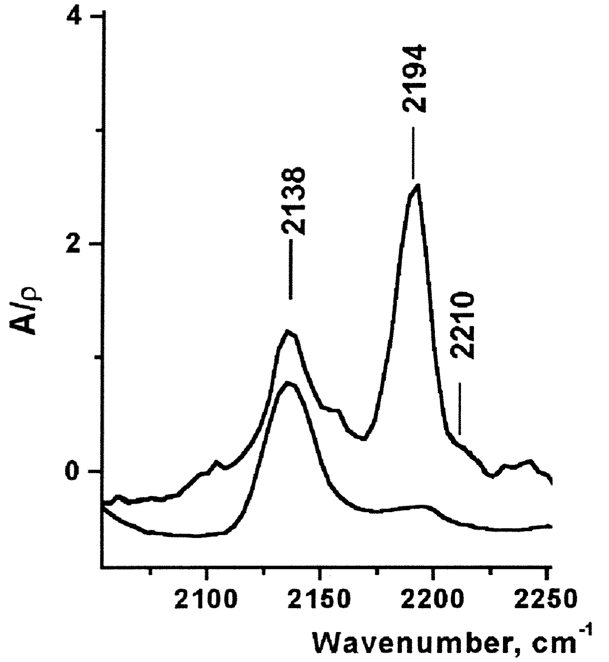

Fig. 2. Difference IR spectra of CO adsorbed at 77K (0.18 Torr): 1 - SiO_2/MAO-1; 2 - SiO_2/MAO-1/Cp_2ZrMe_2 (catalyst A)

So we can conclude:

1. CP_2ZrMe_2 anchors on both W LAS and M LAS of the support SiO_2/MAO;

2. CP_2ZrMe_2 firstly interacts with M LAS of the support.

Active centers of the catalyst SiO_2/MAO/ CP_2ZrMe_2 are formed probably through zirconocene interaction with the most strong LAS.

We have prepared supported catalysts based on CP_2ZrCl_2 and various supports (SiO_2/MAO-1, SiO_2/MAO-2, SiO_2/TMA). LAS content in these supports and catalyst activity at ethylene polymerization have been evaluated. Data of the PE yield vs. LAS-M content for these samples are presented in Fig.3. These data confirm that active centers of the supported zirconocene catalysts are formed through zirconocene interaction with the sites type M LAS.

Table 2. Data on LAS and Zr content in the catalyst SiO_2/MAO-1/Cp_2ZrMe_2 and the support SiO_2/MAO-1

Catalyst	[LAS], μmol/g				*)Δ_{LAS}	[Zr], μmol/g	Zr/Δ_{LAS}	Activity**) kg PE/gZr h
	Support		Catalyst					
	W	M	W	M				
A	49	5	10	0	44	44	1	4.6
B	70	8	51	0	27	26	0.96	14.8

*)$\Delta_{LAS} = [LAS]_{support} - [LAS]_{catalyst}$

**) Polymerization at 80°C, without any cocatalyst

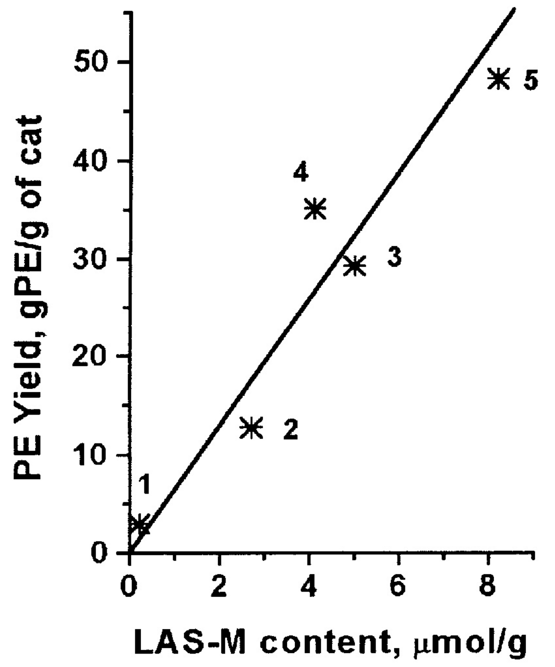

Fig. 3. PE yield vs. M LAS content in the supports SiO_2/ MAO (TMA).

Catalyst used (support/Cp_2ZrCl_2): 1 - SiO_2 (400°C)/TMA; 2 - SiO_2 (400°C)/MAO-2; 3 - SiO_2 (700°C)/MAO-1; 4 - SiO_2 (100°C)/MAO-1; 5 - SiO_2 (400°C)/MAO-1.

Ethylene polymerization at 80°C, in heptane, ethylene pressure 9 bar, $Al(i\text{-}Bu)_3$ as cocatalyst, for 1 hour

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