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Surface vanadium compounds in supported vanadium–magnesium catalysts for ethylene polymerization: X-ray photoelectron and infrared diffusion reflectance spectroscopy studies

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Abstract

Adsorption of NO as a probe molecule in infrared diffusion reflectance spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS) have been used in order to identify surface vanadium species in vanadium–magnesium catalysts (VMC). The presence of V^{3+} and V^{4+} in $VCl_4/MgCl_2$ and V^{4+} in $VOCl_3/MgCl_2$ was shown by XPS and DRIFTS. However, DRIFTS has some limitations due to oxidation of V^{3+} by the reaction with NO; moreover, apparently ions V^{5+} and V^{2+} do not adsorb NO. We have also demonstrated the possible identification of surface ions V^{5+} and V^{2+} in VMC using XPS. Practically in all cases ($VCl_2/MgCl_2$, $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$) one can see a mixture of vanadium ions in different oxidation and coordination states. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium–magnesium catalysts; Ethylene polymerization; X-ray photoelectron spectroscopy; Infrared diffusion reflectance spectroscopy; NO adsorption; Oxidation state of vanadium

1. Introduction

Vanadium–magnesium catalysts (VMC) belong to the well known $MgCl_2$-supported Ziegler–Natta catalysts [1–9]. In addition to high activity, supported VMC exhibit interesting features in polymerization and copolymerization of ethylene with α-olefins: (1) VMC produce polyethylene (PE) with broad molecular-weight distribution (MWD) as compared to PE obtained with the well known titanium–magnesium catalysts (TMC) [4,8,10,11]; (2) VMC provide a higher copolymerizing reactivity at ethylene/α–olefins copolymerization in comparison with TMC [4,12,13]. Nevertheless, the state and structure of the active sites of catalysts are not sufficiently understood yet. One promising way to clarify this problem is provided by the application of modern high-performance analytical techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron spectroscopy (SES). Some reports concerning

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the application of these methods for studying the oxidation state of titanium species in TMC have appeared recently [14–18]. Application of these methods in relation to VMC has been mentioned only in a few reports [4].

In this work we used infrared diffusion reflectance spectroscopy (DRIFTS) and XPS to identify surface vanadium species in VMC.

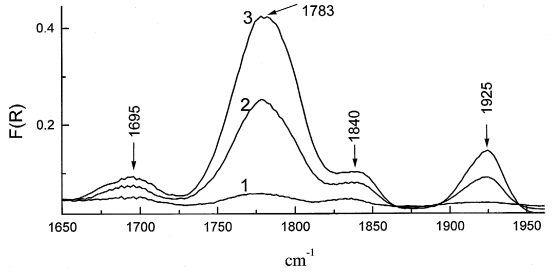

Fig. 2. DRIFTS signals NO on $VCl_4/MgCl_2$ (1.1 wt.% V) surface: (1) $VCl_4/MgCl_2$, (2) $VCl_4/MgCl_2$ with 30 Torr NO. (3) $VCl_4/MgCl_2$ with 35 Torr NO.

2. Experimental

VCl_2 and VCl_3 powders were supplied by Aldrich and used without any purification.

In order to prepare the catalysts ($VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$) we used magnesium chloride, obtained via interaction of magnesium powder with butyl chloride at a mole ratio of $BuCl/Mg = 3$ in heptane at 98°C. The catalysts were prepared by treating the support with excess VCl_4 or $VOCl_3$ in CCl_4 at room temperature followed by repeated washing with heptane. The $VCl_4/MgCl_2$ catalyst contains 1.1 wt.%, and $VOCl_3/MgCl_2$ — 0.88 wt.% of vanadium. Such a method leads to catalysts with high activity [1,10,11].

$VCl_2/MgCl_2$ and $VCl_3/MgCl_2$ samples were prepared by ball-milling of $MgCl_2$ with respective vanadium compound at room temperature for 10 h. The $VCl_2/MgCl_2$ catalyst contains 0.77 wt.%, and $VCl_3/MgCl_2$ — 0.68 wt.% of vanadium.

IR diffuse reflectance spectra of powder were registered with Bruker IFS-113V (equipped with home made diffuse reflectance accessory) in hermetic cell. Nitrogen monoxide was adsorbed at 5 ÷ 100 Torr at room temperature. IR spectra were represented as the Kubelic–Munc function $F(R) = F(R)^{NO} - F(R)^0$; $F(R) = (1 - R)^2/2R$, where R is the reflectance coefficient, and $F(R)^{NO}$ and $F(R)^0$ are the function meaning after and before NO adsorption, respectively.

The XPS measurements of all samples were carried out using a VG ESCALAB ''High Pressure Electron Spectrometer''. The base pressure in the analyzer chamber was typically about 5×10^{-9} Torr. Non-monochromatic MgKα X-ray radiation (1253.6 eV) was used. The pass energy in the hemispherical analyzer was 20 eV for high-resolution spectra and 100 eV for full spectra. The spectrometer energy scale was calibrated with $Au4f_{7/2}$ at 84.0 eV and $Cu2p_{3/2}$ at 932.6 eV. Samples of the catalysts were ground

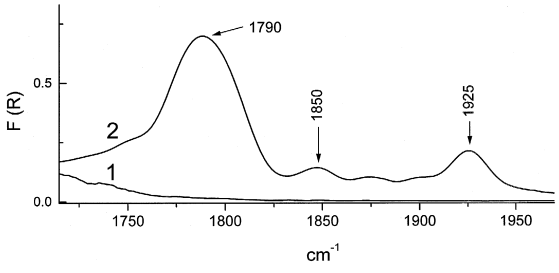

Fig. 1. DRIFTS signals NO on $V0Cl_3/MgCl_2$ (0.88 wt.% V) surface: (1) $V0Cl_3/MgCl_2$, (2) $V0Cl_3/MgCl_2$ with 50 Torr NO.

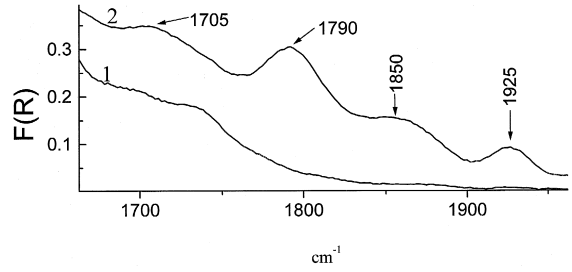

Fig. 3. DRIFTS signals NO on $VCl_3/MgCl_2$ (0.68 wt.% V) surface: (1) $VCl_3/MgCl_2$, (2) $VCl_3/MgCl_2$ with 80 Torr NO.

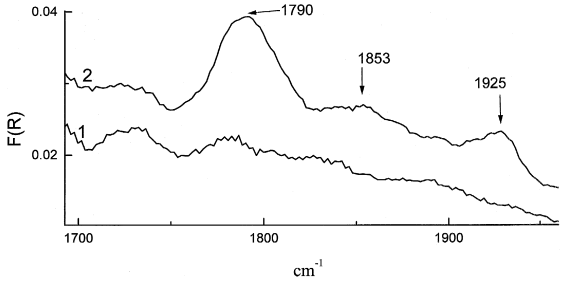

Fig. 4. DRIFTS signals NO on $VCl_2/MgCl_2$ (0.77 wt.% V) surface: (1) $VCl_2/MgCl_2$ (2) $VCl_2/MgCl_2$ with 80 Torr NO.

and mounted on a standard holder by means of double-sided adhesive tape.

3. Results and discussion

In the previous work [19] we have determined a possibility of identification of coordinative-unsaturated ions V^{4+} and V^{3+} on VMC surface by DRIFTS method using NO as a probe molecule. The interaction of NO with V^{4+} leads to appearance of two bands at 1776 and 1920 cm^{-1} in DRIFTS spectra of VMC. We have observed also two bands (1690 and 1840 cm^{-1}) as a result of NO interaction with V^{3+} ions. V^{5+} ions and support ($MgCl_2$) do not adsorb NO. DRIFTS spectra of NO adsorbed on VMC are presented in Figs. 1–4. DRIFTS data for VMC are shown in Table 1. It is interesting to compare our previous DRIFTS data with the XPS results.

XPS was used to characterize the surface of VMC. According to XPS data, all catalysts contain Mg, V, Cl and O. Oxygen found in all samples is attributed to the presence of a small amount of crystalline water, strongly bonded to $MgCl_2$. This water cannot be removed by evacuation under heating and by the reaction with $Al(C_2H_5)_2Cl$ [20]. Two samples, $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$, also contain C, which appeared at the stage of $MgCl_2$ preparation. Most interesting information may be received from XPS observation of the variation in the oxidation state of vanadium species. Decreasing the oxidation state of vanadium was found to induce a chemical shift to lower binding energy of V2p level. V2p level binding energy and the proposed oxidation state of vanadium in VMC are shown in Table 1.

From the analysis of XPS data (Table 1) one can see the presence of two types of vanadium on the surface of $VCl_4/MgCl_2$ (V^{3+} and V^{4+}) and $VOCl_3/MgCl_2$ (V^{5+} and V^{4+}). A part of vanadium is reduced while supporting $VOCl_3$ and VCl_4. Such reduction was previously

Table 1
Data obtained by examining VMC by DRIFTS and XPS

Sample	Vanadium content, wt.%	DRIFTS		XPS	
		ν_{NO}, cm^{-1}	State of vanadium	Binding energy V2p, eV	State of vanadium
$VCl_2/MgCl_2$	0.77	1790 and 1925	V^{4+}	513.5	V^{2+}
		1853[a]		515.8	V^{3+}
$VCl_3/MgCl_2$	0.68	1705 and 1850	V^{3+}	515.8	V^{3+}
		1790 and 1925	V^{4+}		
$VCl_4/MgCl_2$	1.1	1695 and 1840	V^{3+}	515	V^{3+}
		1783 and 1925	V^{4+}	516.5	V^{4+}
$V0C1_3/MgCl_2$	0.88	1790 and 1925	V^{4+}	516.5	V^{4+}
		1850[a]		517.3	V^{5+}
V_2O_3[b]				515.7	V^{3+}
VO_2[b]				516.3	V^{4+}
$VOCl_2$[b]				516.4	V^{4+}
V_2O_5[b]				517.4	V^{5+}

[a] This value of vibration frequencies may be associated with V^{4+}-NO [24].
[b] XPS data for vanadium oxides were obtained from Ref. [23].

demonstrated for $VOCl_3/MgCl_2$ by ESR-spectroscopy [19]. As proposed, the composition of samples $VCl_3/MgCl_2$ and $VCl_2/MgCl_2$ satisfies the requirements. DRIFTS spectroscopy data well agree with XPS in the case of $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$. At the same time, DRIFTS fails in determining the $VCl_3/MgCl_2$ and $VCl_2/MgCl_2$ composition. The presence of V^{4+} on the catalysts surface in the case of $VCl_3/MgCl_2$ and $VCl_2/MgCl_2$ may be associated with a secondary process of NO interaction with vanadium ions. Most probably the reaction results in oxidation of V^{3+} ions. This reaction is well known for vanadium oxides [21,22]. Such reaction leads to the formation of V^{4+} ions being registered in DRIFTS spectra VMC.

According to these results, one can see the importance of XPS and DRIFTS spectroscopy for studying $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$. We have shown the variability of the $VCl_n/MgCl_2$ system. Catalysts $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$ always contain a mixture of vanadium ions in different oxidation and coordination states.

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