

# Preparation and characterization of magnesium oxide-bound trichlorobis(tetrahydrofuran)titanium(III)

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The anchoring of the coordinatively unsaturated complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  to the surface of magnesium oxide leads to the formation of surface attached Ti(III) complexes, which were investigated by e.s.r. and i.r. spectroscopy. It has been found that the anchoring of the original complex to the surface is achieved by the reaction of the complex with the basic centres on the surface of magnesium oxide. On thermal decomposition of thus formed surface complexes their aggregation takes place. By their reaction with oxygen the radical  $\text{O}_2^-$  arises which is coordinated to Ti(IV).

Путем нанесения координационно ненасыщенного комплекса  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  на  $\text{MgO}$  получен закрепленный на поверхности комплекс титана(III). Проведено исследование полученного комплекса методами электронного парамагнитного резонанса и инфракрасной спектроскопии. Показано, что закрепление исходного комплекса на поверхности происходит за счет основных центров оксида магния. При термическом разложении полученных комплексов происходит их агрегация. При взаимодействии с кислородом образуется радикал  $\text{O}_2^-$ , стабилизированный на Ti(IV).

Since titanium complexes are highly active polymerization catalysts, in recent years great attention has been devoted to the syntheses of titanium complexes anchored to inorganic carriers. In most cases the anchoring was achieved by means of hydrolytic reaction of  $\text{TiCl}_4$  [1, 2] or titanium(IV) organic compounds [3] with surface hydroxyl groups of the carrier.  $\text{TiCl}_4$  can be anchored also to the carrier functionalized by aluminiumorganic compounds [1, 2]. The anchoring of Ti(III) complexes to silica functionalized by amino groups is described in [4]. In this case the anchoring was achieved by substitution of the neutral ligands in hexacoordinated Ti(III) complexes. Anchoring of coordinatively unsaturated Ti(III) complexes,

where an addition reaction of the complex with the surface donor atoms can be expected, has not been described yet. In our paper the anchoring of the pentacoordinated complex trichlorobis(tetrahydrofuran)titanium(III)  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  [5] to magnesium oxide is reported. The surface complexes thus prepared were studied by electron spin resonance and infrared spectroscopy, their thermal decomposition and reaction with oxygen were also investigated.

## Experimental

All reactions and operations were carried out in an atmosphere of dry oxygen-free nitrogen in a special all-glass equipment connected to a nitrogen manifold under pressure of about 0.102 MPa [6]. All samples and solvents were sealed under nitrogen in glass tubes.  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  was prepared by thermal decomposition of  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_3$  [7].  $\text{MgO}$  ( $S = 75 \text{ m}^2 \text{ g}^{-1}$ ) was prepared by thermal decomposition of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  at 973 K at reduced pressure (about 1.3 kPa) of hydrogen.

The anchored complexes were prepared by interaction of the carrier (magnesium oxide) with saturated benzene or chloroform solutions of  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$ . The excess complex was washed out from the carrier with pure solvent. The titanium(III) content was determined by titration with Ce(IV) sulfate using ferroin as indicator.

Electron spin resonance spectra were recorded on a Varian E-4 spectrometer at 77 K at microwave frequency 9.1 GHz. The intensity of the spectra was determined by numerical double integration of the experimental spectra. A single crystal of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was used as a standard for quantitative measurement of the Ti(III) concentration.

The thermal decomposition of anchored complexes was studied in sealed e.s.r. tubes in the temperature range 373—473 K. After the sample was heated to the desired temperature, the tube was immediately immersed into liquid nitrogen and the e.s.r. spectrum was recorded. Then the sample was allowed to stand for about 20 min at room temperature and the e.s.r. spectrum was recorded again. The reaction of surface complexes with  $\text{O}_2$  was studied after the sample was exposed to atmospheric oxygen at 77 K, then it was shortly heated to room temperature in an e.s.r. tube and again cooled to 77 K.

For the infrared spectral measurements the preliminarily prepared samples of  $\text{MgO}$  were pressed into the form of discs with "density"  $\rho = 20\text{--}30 \text{ mg cm}^{-2}$ . Preparation of the samples and attachment of the complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  were achieved directly in the vacuum infrared cell. The samples of magnesium oxide were heated under hydrogen at 723 or 973 K with subsequent evacuation at this temperature for 2 h at the pressure of  $1.3 \times 10^{-2} \text{ Pa}$ . Some samples were heated at 973 K in the absence of hydrogen at the pressure of  $1.3 \times 10^{-2} \text{ Pa}$ .

The adsorption of benzonitrile and deuteriochloroform was used for characterization of acid-base properties of the  $\text{MgO}$  surface. Based on the formation of hydrogen bonds between the hydroxyl groups on the surface and the above-mentioned adsorbates, the proton-donor ability of the hydroxyl groups was expressed in terms of proton affinity  $PA$ . (For the surface hydroxyl groups the  $PA$  is the enthalpy of the addition of the proton to the atom  $\text{O}^-$  on the surface in vacuum.)  $PA$  was calculated by the methods reported in [8].

Changes in the position of the bands  $\tilde{\nu}(\text{CD})$  in the spectrum of deuteriochloroform make it possible to express the strength of the basic surface centres in terms of the scale  $\text{p}K_{\text{a}}$  according to the calibration graph from [9]. Deuteriochloroform and benzonitrile were allowed to adsorb at room temperature for 3 and 15 min, respectively, without removing subsequently the adsorbates from the gaseous phase.

The anchoring of the complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  took place in a saturated benzene solution in an infrared cell within 15–30 min. The excess complex was then washed out with benzene. The rest of gaseous benzene was removed by evacuation to the pressure of  $1.3 \times 10^{-2}$  Pa. With the aim of determining the exact site of attachment of the surface complex, also deuteriochloroform was adsorbed on these samples.

Infrared spectra in the range 1100–4000  $\text{cm}^{-2}$  were recorded on a UR-20 spectrometer at room temperature. Spectra recorded in the transmittance  $T$  scale were transformed into the scale

$$D_{\nu} = \log \frac{T_0(\nu)}{T(\nu)}$$

where  $T_0(\nu)$  is the background transmittance, which was transformed into zero background and standardized to the "density"  $\rho$ .

## Results and discussion

### *Acid-base properties of magnesium oxide*

In the infrared spectra of MgO heated at 723–973 K the band  $\tilde{\nu}(\text{OH}) = 3750 \pm 10 \text{ cm}^{-1}$  occurs, which is assigned to the isolated MgOH groups. The band of strongest intensity is produced by the sample heated at 723 K. On deuteriochloroform adsorption this band is shifted by 10–20  $\text{cm}^{-1}$  into the range of lower frequencies. On benzonitrile adsorption the shift makes 70  $\text{cm}^{-1}$ . According to [8], to these OH groups the values of  $PA$   $1.6 \times 10^6 \pm 0.05 \times 10^6 \text{ J mol}^{-1}$  pertain, which is in good agreement with literature data on nonacid character of these OH groups [10].

In the spectrum of the adsorbed benzonitrile the band  $\tilde{\nu}(\text{CN})$  is shifted by 31  $\text{cm}^{-1}$ , which corresponds to formation of the coordination bond with the  $\text{Mg}^{2+}$  cations on the surface [11].

On the adsorption of deuteriochloroform the formation of two  $\tilde{\nu}(\text{CD})$  bands, at 2195 and 2245  $\text{cm}^{-1}$ , respectively, was observed for all samples (Fig. 1). This corresponds to two base centres on the surface as reported in [9]. There are  $\text{p}K_{\text{a}} = 11 \pm 2$  centres of the first type ( $\tilde{\nu}(\text{CD}) = 2195 \text{ cm}^{-1}$ ), *i.e.* as regards the basicity these centres are analogous to aliphatic amines. It can be assumed that

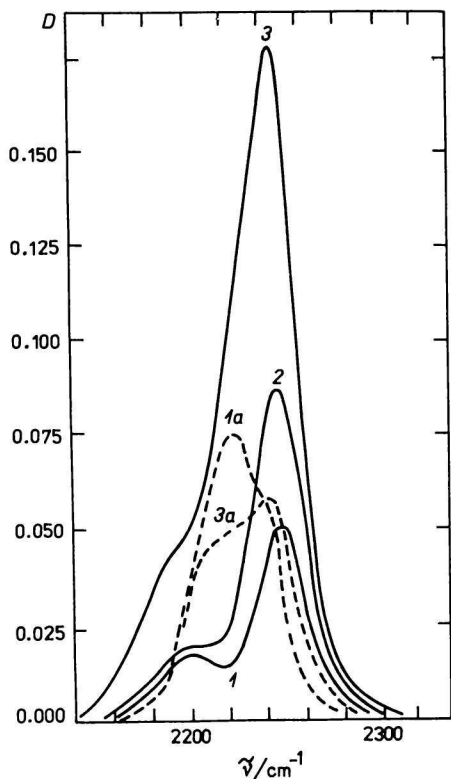


Fig. 1. Infrared spectra of adsorbed deuteriochloroform.

1. Adsorbed on MgO heated at 723 K in H<sub>2</sub>;
  2. adsorbed on MgO heated at 973 K in H<sub>2</sub>;
  3. adsorbed on MgO heated at 973 K *in vacuo*.
- Curves *a* are the i.r. spectra obtained after adsorption of CDCl<sub>3</sub> on MgO with anchored TiCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub>.

these centres belong to bridging O<sup>2-</sup> ions on the magnesium oxide surface. The value of pK<sub>a</sub> of the second type of centres is +1. As for the concentration of base centres, all investigated centres differ no more than by two- to threefold.

### Investigation of the anchored complexes

TiCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub> is soluble in benzene or in chloroform and a green solution is formed. The solubility is greater in chloroform ( $6.7 \times 10^{-5}$  mol g<sup>-1</sup> Ti(III)) than in benzene ( $1.2 \times 10^{-5}$  mol g<sup>-1</sup> Ti(III)). Because of rapid spin-lattice relaxation the e.s.r. spectra can be observed only at 77 K. Due to exchange interactions Ti(III)...Ti(III) the benzene solution shows only a singlet with  $g_0 = 1.91$  at 77 K (Fig. 2a). In chloroform solution the parameters of rhombic e.s.r. spectra (Fig. 2b) are  $g_1 = 1.80$ ,  $g_2 = 1.89$ ,  $g_3 = 1.98$ ,  $\bar{g} = 1.89$ . The Ti(III) concentration calculated from the intensity of e.s.r. spectra corresponds to the Ti(III) concentration determined by chemical analysis, *i.e.* the complex TiCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>2</sub> occurs in solution in monomeric form.

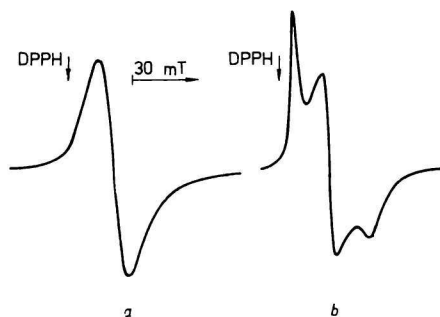


Fig. 2. Electron spin resonance spectra of  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  solutions *a*) in benzene, *b*) in chloroform.

On the basis of electronic spectra of this complex, both in solid and liquid phase, Ti(III) appears to be pentacoordinated [5, 12]. As described in [13],  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  reacts with  $\text{CH}_3\text{CN}$  and  $[\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2(\text{CH}_3\text{CN})]$  is formed. A complex  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{TiBrCl}_3(\text{C}_4\text{H}_8\text{O})_2]$  is obtained after the reaction of  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  with  $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Br}$  [14]. In both cases the coordination number of originally pentacoordinated, coordinatively unsaturated complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  is completed to six. In such a case it can be assumed that the coordinatively unsaturated complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  is capable also of addition reactions with the donor atoms on the surface of the inorganic carriers.

Chemical analysis showed that 0.6% of Ti(III) in the form of a complex is anchored to the surface of MgO. The surface Ti(III) complex shows axial e.s.r. spectra with  $g_\perp > g_\parallel$  (Fig. 3a). As it was not possible to determine the exact values of  $g_\perp$  and  $g_\parallel$  only  $g_0 = 1.93$  was determined. The higher value for  $g$  factor of surface complex in comparison with polycrystalline and dissolved  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  can be explained by an increasing ligand field asymmetry around Ti(III) [15]. The width of the e.s.r. spectrum ( $\Delta H = 10.0$  mT) indicates the presence of more than one type of Ti(III) complex on the surface of the carrier. The parameters of e.s.r. spectra are similar to those of chlorotitanium(III) complexes anchored to functionalized silica [4] and they correspond to hexacoordinated Ti(III) complexes [15, 16]. The concentration of Ti(III) determined from the intensity of e.s.r. spectrum corresponds to the concentration determined by chemical analysis, i.e. Ti(III) forms magnetically diluted complexes on the surface of the carrier.

In the infrared spectra of  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  anchored to MgO which was heated at 723 and 973 K, several absorption bands at 1190, 1480, 2880, 2920, 2960, and 2990  $\text{cm}^{-1}$  appear; these can be attributed to vibrations of tetrahydrofuran. Weaker bands appearing at 1520, 1620, 3035, 3050, 3100, and 3130  $\text{cm}^{-1}$  can be assigned to vibrations of the benzene ring. When MgO heated at 723 K was used as a carrier, also changes in the spectrum of the hydroxyl groups were observed, the intensity of the band at 3750  $\text{cm}^{-1}$  was lowered and broad bands at 3680 and 3580  $\text{cm}^{-1}$  appeared. Under vacuum ( $10^{-2}$  Pa) neither the benzene nor tetrahydrofuran molecules, which possibly were formed as a consequence of destruction

of the starting titanium complex, can form hydrogen bonds with the MgOH groups. For this reason we can assume that the perturbation of OH groups is due to their interaction with the anchored complex, most probably through the mechanism of hydrogen bond to chlorine atoms from complexes attached to adjacent basic centres.

The adsorption of deuteriochloroform onto the magnesium oxide supporting the anchored complex caused formation of an absorption band  $\tilde{\nu}$ (CD) at  $2220\text{ cm}^{-1}$ , whereas the band  $\tilde{\nu}$ (CD) at  $2195\text{ cm}^{-1}$  pertinent to the starting magnesium oxide disappeared and the intensity of the band  $\tilde{\nu}$ (CD) at  $2245\text{ cm}^{-1}$  was considerably decreased (see curves 1 and 1a, 3 and 3a; Fig. 1). The band  $\tilde{\nu}$ (CD) at  $2220\text{ cm}^{-1}$  is assigned to base centres with  $\text{p}K_{\text{a}} = +7$ , i.e. to centres which did not exist in the starting state of magnesium oxide. On the basis of these results it can be assumed that the surface basic centres are responsible for the attachment of the complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  to the surface of magnesium oxide.

### *Some properties of the anchored complex*

As a consequence of thermal decomposition of the complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  attached to MgO the e.s.r. signal became less intensive, but the shape of the line remained unchanged. After heating to  $373\text{ K}$  the intensity of e.s.r. spectra was 88% of the original intensity before thermal decomposition and after heating to  $473\text{ K}$  this intensity was 48% of the original. On temperature increase the coordinated tetrahydrofuran is released from the anchored complex and most probably also formation of e.s.r. inactive Ti(III) aggregates takes place.

This process could not be reversed by the reaction with tetrahydrofuran vapours at room temperature. However, since the temperature of the thermal decomposition is comparatively low ( $373\text{--}473\text{ K}$ ), we do not assume any migration of Ti(III) from the surface into the bulk of the carrier.

The anchored Ti(III) complexes are highly reactive towards oxygen. The reaction with  $\text{O}_2$  was followed by an intensity decrease of Ti(III) e.s.r. signal and

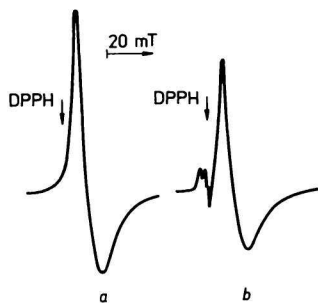
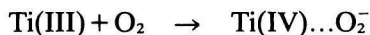


Fig. 3. Electron spin resonance spectra of  
*a*) complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  anchored on MgO,  
*b*) anchored complex after the reaction with  $\text{O}_2$ .

a new signal appeared (Fig. 3b). The parameters of this new signal are  $g_1 = 2.002$ ,  $g_2 = 2.007$ ,  $g_3 = 2.022$ . This signal can be attributed to  $O_2^-$  radical [17, 18]. As  $g_3 < 2.03$  the  $O_2^-$  radical is coordinated on a cation with formal charge +3 or higher [19]. The reaction with oxygen can be represented by the following scheme



The coordinated radical  $O_2^-$  was stable only at 77 K, at the room temperature the e.s.r. of  $O_2^-$  disappeared after a short time.

No formation of  $O_2^-$  radical was observed after a reaction of  $O_2$  with Ti(III) aggregates formed by the thermal decomposition of anchored Ti(III) complexes.

In summary, our experimental results show that the coordinatively unsaturated complex  $\text{TiCl}_3(\text{C}_4\text{H}_8\text{O})_2$  is capable to react with the basic centres of inorganic carriers, e.g. of magnesium oxide, in a similar way as it reacts with acetonitrile [13] or  $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Br}$  [14] and thus form hexacoordinated surface titanium(III) complexes. These conclusions are confirmed by the data obtained by two independent methods of investigation, i.e. by e.s.r. and i.r. spectroscopy.

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