Journal of Organometallic Chemistry, 269 (1984) 29–37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CARRIER INFLUENCE ON THE PARAMAGNETIC AND CATALYTIC PROPERTIES OF SUPPORTED TITANIUM COMPLEXES

WINCENTY SKUPIŃSKI* and IWONA CIEŚLOWSKA-GLIŃSKA

Department of Chemistry, Technical University — Politechnika, 00 662 Warszawa, Koszykowa 75 (Poland)

(Received February 28th, 1984)

Summary

Alumina-silica possessing various Al_2O_3/SiO_2 ratios was used as a carrier of surface titanium complexes. The systems obtained were examined as models for the investigation of the macroligand (inorganic gel) influence on the physicochemical properties of supported transition metal complexes. The titanium complexes were prepared first by the reaction of $CpTiCl_3$ with the hydroxyl groups of the gel and then reduced by an excess of BuLi. The influence was established of the basic gel properties on: (a) the amount of titanium(IV) and titanium(III) complexes on the alumina-silica gel surfaces; (b) the symmetry of the surface Ti^{III} surface complexes; (c) the electron density around the surface-Ti^{III} ions, ionic or covalent bonds character in a complex; and (d) the catalytic activity in olefin hydrogenation.

Introduction

Alumina-silica gels have different structures and, different amounts and strengths of the acidic and basic sites on their surfaces depending on the Al_2O_3/SiO_2 ratio [1,2]. All these different sites and different structures should have a very important influence on the physicochemical properties of transition metal supported complexes.

This influence was observed for π-allylnickel complexes when their catalytic activity in diene polymerization was shown to depend on the acidity of the alumina-silica gel [3], and their selectivity to 1,4-*cis*- or 1,4-*trans*-polydiene formation, on the amount of SiO_2 in the gel [4]. To see what the influence of the alumina-silica properties is on other transition metal supported complexes, we used the same alumina-silica gels for preparing systems containing titanium(IV) and titanium(III) surface compounds. The physicochemical and catalytic properties of these systems are presented in this paper.

0022-328X/84/$03.00

Experimental

Alumina-silica gels were obtained by co-precipitating the corresponding hydroxides from an isopropanol solution of tetraethoxysilane (Fluka; pure grade) and aluminium isopropoxide (POChem; pure), using distilled water as the precipitating agent. After washing, the gels were dried at 313, 353 and 393 K for 24 h at each temperature and then calcined for 24 h at 873 K.

The 1.02–0.5 mm grain fraction was used for catalyst preparation. The stoichiometries of the gels were determined by measuring the amount of Al_2O_3 remaining after reaction of HF with the gel sample (Al_2O_3–SiO_2 + HF → Al_2O_3 + $SiF_4{}^{\uparrow}$). The specific surface areas of the alumina-silica samples were determined by gas chromatography. The concentrations of surface hydroxyl groups were determined using sodium naphthalide solution titration. Surface acidity and basicity were measured by butylamine or benzoic acid solution titration, respectively, in the presence of Hammett indicators.

Prior to reaction with $CpTiCl_3$ (Strem, pure), the gel samples were heated (24 h) in a stream of argon at 873 K. $CpTiCl_3$ was added to the cooled gel grains in benzene solution at room temperature with the stoichiometry to the surface hydroxyl groups being 1/1. After several hours, depending on the ratio of the alumina-silica sample (from 6 h for alumina to about 24 h for silica), the reaction was completed. HCl evolved was trapped in sodium hydroxide solution and determined by titration of excess NaOH.

For reaction with an excess of $CpTiCl_3$, unreacted titanium compounds were washed out with benzene. Durably bonded titanium complexes were removed from the gel surface with nitrous acid, whereby the amount of durably bonded complexes to the surface titanium complexes was determined. All titanium compounds were oxidized to titanium(IV) ions and determined by colorimetry using H_2O_2 solution.

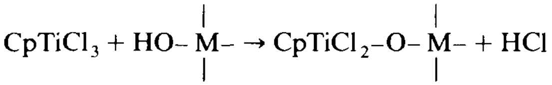
Catalysts possessing titanium(IV) surface complexes were reduced with a 10-fold excess of BuLi in hexane. The colour of the grains changed to black, and some black titanium compounds transferred from the grain surface to the solution over the gels. After 2 h, the catalyst grains were washed several times with hexane until the solution over the grains was colourless, and they were then dried under vacuum. ~ 0.1 g of such prepared catalysts was used in the ethylene, propylene and isobutylene hydrogenation in a static reactor (200 ml volume), which was equipped with a mercury manometer for monitoring hydrogen consumption. Reactions were carried out at room temperature for ethylene and propylene, and at 343 K for isobutylene. The hydrogen/olefin ratio was 4/1.

The catalyst samples were investigated by the EPR method using a 200 WROCŁAW spectrometer with Mn^{2+} in MgO as internal standard. All operations beginning from the reaction of $CpTiCl_3$ with the hydroxyl groups of the gel were carried out in an argon atmosphere using dry and deoxidized solvents.

Results and discussion

(a) Surface titanium(IV) complexes

The investigated catalysts were prepared in two steps. First, $CpTiCl_3$ was treated with the alumina-silica surface hydroxyl groups according to reaction 1:



$$CpTiCl_3 + HO-\underset{|}{\overset{|}{M}}- \rightarrow CpTiCl_2-O-\underset{|}{\overset{|}{M}}- + HCl \qquad (1)$$

$(M = Al, Si)$

The stoichiometry of this reaction was supported by measurements of the amount of: (a) unreacted titanium complexes when an excess of them was used; (b) titanium durably bonded to the gel surface; and (c) HCl evolved during the reaction.

The results obtained indicated that not all the hydroxyl groups reacted with $CpTiCl_3$; only one surface hydroxyl group reacted with one $CpTiCl_3$ molecule. The amounts of titanium complexes bonded to the surfaces of the investigated gels and their amounts of hydroxyl groups and specific areas are presented in Table 1. About 75% of all surface hydroxyl groups of 100, 80, 62 and 42% Al_2O_3 gels and only about 10% of the surface hydroxyls of 18 and 0% Al_2O_3 gels reacted with $CpTiCl_3$.

The amounts of the surface OH groups were measured by titration with the sodium naphthalide molecule, whose dimensions are comparable with the $CpTiCl_3$ molecule (0.2 nm^2) [5,6]. Therefore we should expect all the determined hydroxyls of the gels used to be accessible for $CpTiCl_3$ and any steric hindrance not to influence reaction 1.

The reactivity of $CpTiCl_3$ towards protons depends on their acidity and the presence of a Lewis base which can bind the HCl produced during the reaction [7,8]. On comparing the acid–base properties of the investigated gels with the activity of the alumina-silica hydroxyl in reaction 1 (measured by the yield of surface titanium(IV) complexes, see Figs. 1 and 2), it may be said that the basic properties of the gel are more important in this reaction than the acidity of the hydroxyl groups. The pure silica gel and the 18% Al_2O_3 gel, which do not have strong basic sites but have neutral OH groups, SiO_2 or strong Brønsted acidic hydroxyls, on the ~ 20% Al_2O_3 gel [1,2] are almost inactive in the reaction with $CpTiCl_3$. The rest of the gels characterized by strong basic properties are highly active. The basic properties of the gel not only influence the yield of the surface titanium complexes positively, but also affect the rate of reaction 1, which is about four times slower on silica than on alumina.

The supported titanium complexes obtained in the first step (reaction 1) were inactive in olefin hydrogenation and did not produce any ESR signals.

TABLE 1

ALUMINA-SILICA SPECIFIC AREAS, HYDROXYL GROUPS AND CONCENTRATIONS OF CYCLOPENTADIENYL SURFACE TITANIUM(IV) COMPLEXES

	Alumina/Silica (w/w %, Al_2O_3/SiO_2)					
	100/0	80/20	62/38	46/54	18/82	0/100
Specific area (m^2/g)	212	218	160	155	137	73
OH concentration (OH/g)	0.10	0.18	0.22	0.08	0.20	0.16
OH concentration (OH/nm^2)	0.3	0.5	0.8	0.2	1.1	1.3
mmol Ti complexes (mmol/g of carrier)	0.075	0.14	0.17	0.06	0.016	0.023
mmol Ti complexes/OH groups (%)	75	78	75	75	6.4	14.4

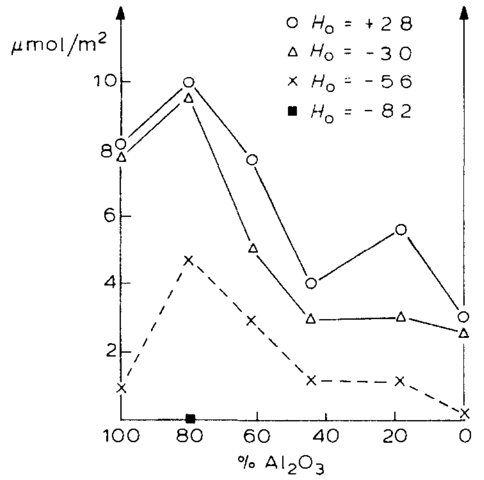


Fig. 1. The acidity (Hammett scale) of silica-alumina

(b) Surface titanium(III) complexes

The surface titanium complexes obtained in the first step were modified by adding a 10-fold excess of BuLi in hexane. The orange-yellow colour of the grains changed to grey-black to dark brown, depending on the gel. Some of the titanium complexes transferred from the grain surface to the hexane solution as a result of titanium surface–oxygen bonds breaking, where besides alkylation of Ti–Cl bonds, alkylation of Ti–O bonds also occurred. In this way, the prepared catalysts gave anisotropic ESR singlets characteristic of titanium(III) ions [9], and were active in α-olefin hydrogenation.

Typical anisotropic axial powder titanium(III) ion ESR signals were obtained for all the investigated systems containing 100, 80, 62, 46 and 0% Al_2O_3. Only for the

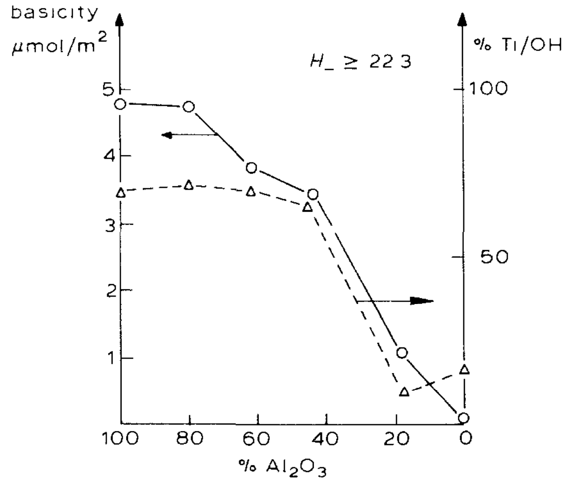


Fig. 2. The basicity (Hammett scale) of silica-alumina and the ratio of titanium(IV) surface complexes to initial hydroxyl groups.

TABLE 2

$g_\perp$ AND $g_\parallel$-FACTORS AND RELATIVE INTENSITY OF ESR SPECTRA

		Alumina/Silica (w/w %, Al_2O_3/SiO_2)					
		100/0	80/20	62/38	46/54	18/82	0/100
$g_\perp$	–	1.9880	1.9900	1.9923	1.9999	–	1.9846
$g_\parallel$	–	1.9618	1.9595	1.9818	1.9825	–	1.9797
Relative intensity	(au/g)	7.25	6.50	3.00	1.10	0	1.00

18% Al_2O_3 gel was the amount of titanium(III) complexes too small to be detected. The relative amounts of the supported titanium(III) complexes determined by integration of the ESR signals are presented in Table 2.

This table shows that the amount of supported titanium(III) complexes decreases with decreasing Al_2O_3 content in the investigated gels, which can be correlated with decreasing gel basicity.

The quantities of the titanium(III) complexes obtained are different from the initial quantities of titanium(IV) complexes, which were greatest on the 80 and 62% Al_2O_3 gels. Comparing the amounts of titanium(IV) and titanium(III) complexes in the function of the gel basicity (see Figs. 2 and 3), we may say that the amount of titanium(III) obtained correlates better with gel basicity than the amount of titanium(IV) complex.

The quantity of the stable titanium(III) surface complexes supported on alumina-silica should depend mainly on the following factors: (a) The ability of the titanium(IV) surface complexes to be reduced to titanium(III) complexes; (b) the resistance of the titanium(III) complexes obtained to be reduced to lower oxidation states; (c) alkylation of titanium-surface lattice oxygen bonds of titanium(IV) and titanium(III) complexes which causes breaking of the titanium–support bonds and in this way removes titanium complexes from the gel surface and decreases the potential amount of titanium(III) complexes.

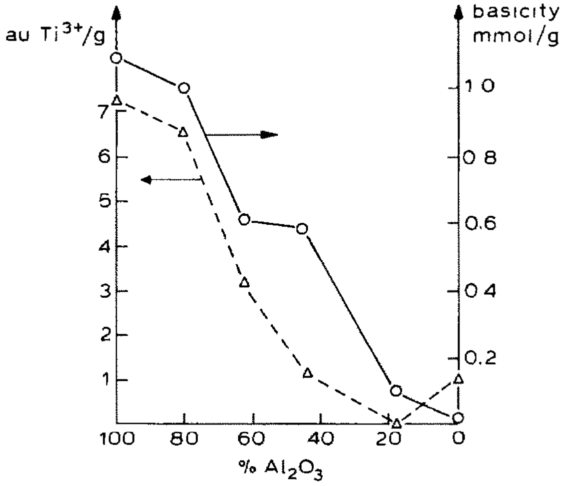


Fig. 3. Basicity of alumina-silica ($H_- \geqslant 22.3$) and the relative concentration of titanium(III) surface complexes.

Measurements of the titanium complexes removed from the gel surface during reduction indicated that about 60% of the initial amounts of titanium complexes remained on all the investigated gels after reduction. This means that gel basicity or acidity does not influence titanium–oxygen bond alkylation. Gel basicity must influence titanium(IV) → titanium(III) reduction or influence further reduction of titanium complexes to lower oxidation states in a way that aids reduction to titanium(III) complexes whilst preventing further reduction, thus giving as a result the largest amount of stable titanium(III) complexes on the most basic gels.

(c) EPR spectra of the titanium(III) surface complexes supported on alumina-silica

All the obtained anisotropic axial titanium(III) EPR signals of the investigated systems have $g_{\perp} > g_{\parallel}$ (see Fig. 4). The values of $g_{\perp}$ and $g_{\parallel}$ and the signals widths are given in Table 2. The ΔH-values of all the signals are larger than 10 mT which indicates the presence of more than one type of titanium(III) surface complex on all the gels investigated [10]. High values of the $g_{\perp}$ and $g_{\parallel}$-factors near the value of the g factor of a free electron suggest tetrahedral symmetry with tetragonal distortion of the surface titanium(III) complexes obtained. $g_{\perp}$ and $g_{\parallel}$ values decrease when the gel basicity increases. The change is greater for the $g_{\parallel}$-value indicating strong interactions between the titanium(III) ions and the ligands in the surface complexes [11].

The decreasing $g_{\parallel}$-values for the investigated systems according to the following equation:

$$g_{\parallel} = g_e - \frac{8\lambda}{\Delta}\alpha^2 \qquad (2)$$

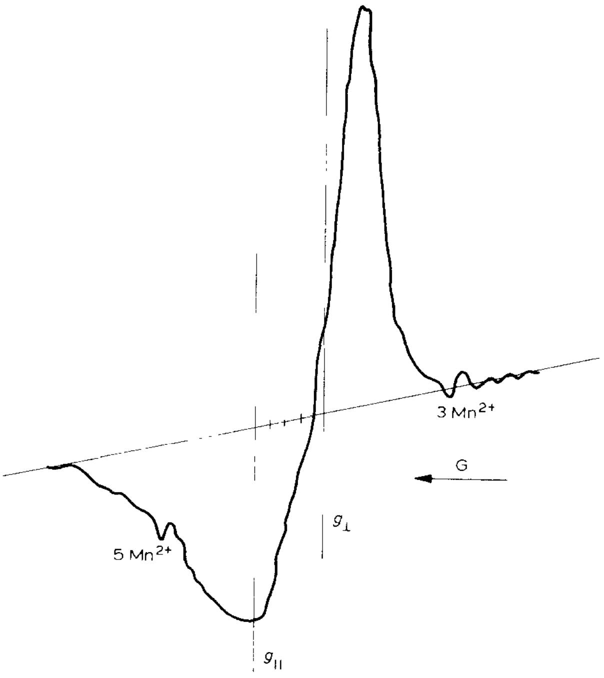


Fig. 4. EPR signal of Ti^{III} ions on 80% Al_2O_3 alumina-silica.

(where $g_e = 2.0023$; λ is the spin-orbit coupling; $\Delta = E_{x^2-y^2}$, the E_{xy} d orbital energy gap; and α is the probablity of the unpaired electron staying on the Ti^{III} ion in a complex, (the grade of ionic character of metal–ligand bonds) must be connected with a lowering of complex symmetry-decreasing Δ-value and more ionic character of the titanium ligands bonds. In the case of relatively high values of $g_{\|}$, the opposite situation must apply.

The low symmetry of the titanium complex structure must be the result of strong interaction between the titanium ions and the support surface. Cyclopentadienyltitanium compounds can form five- or six-coordinated complexes but only when the ligands are small and have relatively strong Lewis base character [12]. Lattice surface oxygen anions, which can be very strong Lewis base sites, form complexes with the surface titanium complexes [9,13], thus titanium(III) complexes complexed by lattice surface oxygen anions can exist on the most basic gels investigated and they are responsible for the low values of $g_{\|}$.

Thus we may expect the presence of four-, five- and even six-coordinated titanium(III) surface complexes on the most basic alumina-silica gels in the systems which we have investigated.

Basic sites can also influence the bond covalency in the surface complexes of titanium(III). EPR investigation of titanium(III) compounds complexed by aluminium chloroalkyls possessing changing donor properties [14] proved the decrease in unpaired electron delocalization from the titanium ion to other ligands when the donor properties of aluminium chloroalkyls increased. The same effect should be observed in our investigated systems. Complexation of titanium(III) ions with strong basic surface oxygen anions should prevent the electron delocalization from the titanium ion to the ligands. This effect increases the α-value in equation 2 and is responsible for the lower $g_{\|}$-value.

Because it is impossible to judge which effect makes the g-values lower (symmetry lowering or covalency lowering in our investigated systems), we must assume that both these effects are operating when titanium(III) complexes are supported on the most basic alumina-silica gels. The opposite picture should apply to the neutral or acidic alumina-silica gels (pure silica and 20% Al_2O_3 alumina-silica). There should be "more tetrahedral" with more covalent bonds titanium(III) surface complexes which should be characterized by relatively higher $g_{\|}$-values.

(d) Olefin hydrogenation

The systems obtained by reduction of the surface cyclopentadienyltitanium(IV) complexes (I) with BuLi were tested as catalysts for ethylene, propylene and isobutylene hydrogenation. Whereas ethylene and propylene could be hydrogenated at 293 K, isobutylene needed a temperature of 343 K to be hydrogenated with a similar efficiency. The results obtained are presented in Table 3.

The activity of the catalyst, measured as ml of H_2 consumed per minute and amount (g) of catalyst, increased in parallel with increasing basicity of the supports used, the most efficient catalyst has pure alumina. As we mentioned before, we should expect the presence of titanium surface complexes with various oxidation states of the metal on the alumina-silica gels. Furthermore, the surface complexes having ions with different oxidation states from +3 should be on the less basic gels; the greatest amount of the surface titanium(III) complexes are on the most basic gels.

TABLE 3

CATALYTIC ACTIVITY OF THE SUPPORTED TITANIUM COMPLEXES

Olefin		Alumina/Silica (w/w %, Al_2O_3/SiO_2)					
		100/0	80/20	62/38	46/54	18/82	0/100
Ethylene[a]	(ml H_2/g)	8.9	3.57	4.17	4.32	–	1 4
Ethylene[a]	(ml H_2/au Ti^{III})	1.23	0.55	1.39	4.0	–	1 4
Propylene[a]	(ml H_2/g)	7 69	5.88	4.35	4 15	0.3	1.35
Propylene[a]	(ml H_2/au Ti^{III})	1.06	0.90	1.45	3.9	–	1.35
Isobutylene[b]	(ml H_2/g)	5.5	2 5	1.7	–	–	2 22
Isobutylene[b]	(ml H_2/au Ti^{III})	0.76	0.39	0.60	–	–	2.22

[a] Temperature 293 K. [b] Temperature 333 K

The results obtained that the most active catalysts have the greatest amount of titanium(III) complexes indicate the influence of titanium(III) complexes in olefin hydrogenation in our investigated systems.

Supporting this assumption, the activity calculated in ml of H_2 consumed per unit of titanium(III) present in the catalytic system per minute should say more about the catalytic activity of an individual titanium(III) complex. Calculated in this way, the activity as a function of the support composition is presented in Fig. 5. The most active titanium(III) complexes are supported on alumina-silica having ~ 50% Al_2O_3.

This activity cannot be correlated with any physicochemical properties such as basicity, acidity or number of hydroxyl groups, but when we correlate this activity with the $g_{\parallel}$-factor values of the Ti^{III} EPR signals of the investigated systems full agreement is found (see Fig. 5). This suggests that the surface titanium complex structure and bond covalency (in our case tetrahedral symmetry and more covalent bonds in the complex) are responsible for the activity of titanium(III) ions in olefin hydrogenation.

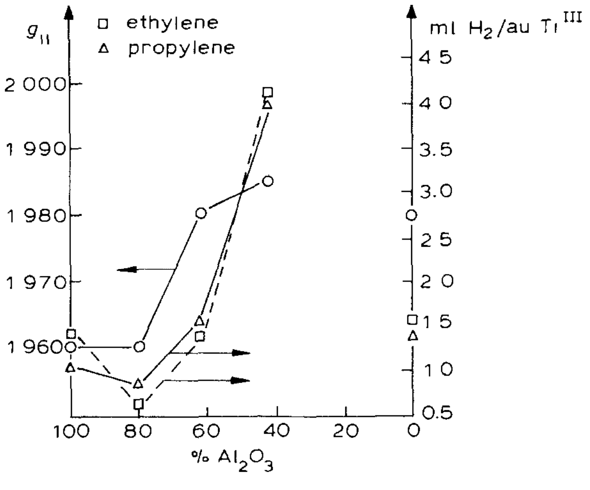


Fig. 5. Initial rate of olefin hydrogenation over titanium-supported complexes and $g_{\parallel}$-values of Ti^{III} ions as a function of Al_2O_3 content in alumina-silica.

References

1 E. Fedoryńska, T. Woźniewski and S. Malinowski, J. Call. Inter. Sci., 69 (1979) 469.
2 J.P. Damon, B. Delmon and J.M. Bonier, J. Chem. Soc. Faraday Trans. I, 73 (1977) 372.
3 W. Skupiński, M. Zawartko and S. Malinowski, React. Kinet. Catal. Lett., 13 (1980) 319.
4 W. Skupiński, M. Zawartko-Laskowska and S. Malinowski, Bull. Acad. Polon. Sci. Ser. Chim. XXVI/I Do 2, 1980, p. 97.
5 R.H. Grubbs, C.P. Lan, R. Cukier and C.H. Brubaker, Jr. J. Am. Chem. Soc., 99 (1977) 4517.
6 J.B. Hendrickson, D.J. Cram and G.S. Hammond, Organic Chemistry 3rd Edition-McGraw-Hill, New York, 1970.
7 W. Skupiński and A. Wasilewski, J. Organomet. Chem. 220 (1981) 39.
8 H. Suzuki and T. Talciguski, Bull. Chem. Soc. Jpn., 48 (1975) 2460.
9 J. Skupińska and W. Skupiński, React. Kinet. Catal. Lett. 16 (1981) 297.
10 J.E. Wertz and J.R. Bolton, Electron Spin Resonance, McGraw-Hill, New York, 1972.
11 I.N. Marov and N.A. Kostromina, EPR and NMR in Chemistry of Coordinated Compounds, Nauka, Moscow, 1979.
12 R.S.P. Coults and P.C. Wailes, Aust. J. Chem. 21 (1969) 2199.
13 G. Plesch, E.A. Panksitz, E.S. Sanko, S. Rapidova, E.N. Yurchenko and M. Zikmund, Chim. Zvesti, 35 (1981) 613.
14 A.E. Volfson and L.N. Garunk, Usp. Khim. 31 (1965) 1648.