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STUDY OF WATER, METHANOL AND ISOPROPANOL ADSORPTION ON THE SURFACE OF TITANOSILICAS OF DIFFERENT STRUCTURE

E. M. Pakhlov[*], *E. F. Voronin, M. V. Borysenko and G. R. Yurchenko*

Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Prospekt Nauki 31
03039 Kyiv, Ukraine

Abstract

The adsorption of water, methyl and *i*-propyl alcohol vapours has been studied on the surface of titanosilicas produced by various methods, as well as on the surface of pure silicon and titanium oxides. Based on findings of the studies, it was concluded that the presence on the surface of pyrogenic titanosilicas (TAS) of hydrolytically unstable Si–O–Ti bonds is responsible for their increased adsorption activity towards water molecules. A dissociative adsorption of H_2O on titanosiloxane bridges is accompanied by an appearance of additional groups ≡SiOH and ≡TiOH, which, in turn, become sites of adsorption of subsequent water molecules.

Keywords: adsorption, CVD-method, surface modification, titanosilicas

Introduction

Synthetic pyrogenic titanosilicas produced by a combined high-temperature hydrolysis of vapours of silicon and titanium tetrachlorides – titanoaerosils (TAS) are prospective fillers of composite materials. Such titanosilicas represent mixed systems consisting of amorphous (SiO_2) and crystalline (TiO_2) phases, which are interconnected by titanosiloxane bonds Si–O–Ti [1, 2]. Some changes observed in parameters of a unit cell of titanium dioxide in titanosilica (both as anatase and rutile) as compared to samples of a pure pyrogenic TiO_2 are explained by the dislocation of a certain number of silicon atoms in lattice internodes of TiO_2 [3]. In addition, it is suggested that [4, 5] titanium ions, for which an octahedral coordination is characteristic, must considerable local perturbations of the nearest silicon–oxygen surrounding, as a result of which, the appearance of different defect sites may be expected which are capable of influencing adsorption processes on the surface of titanosilicas.

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[*] E-mail: user@surfchem.freenet.kiev.ua

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Experimental

The purpose of the present study was to investigate adsorption of water, methanol and propanol-2 vapours on the surface of pyrogenic titanosilicas and pure silicon and titanium oxides. Molecules of these adsorptives possess close electron-donating properties but differing geometric dimensions. Characteristics of studied oxides are given in Tables 1 and 2.

Titanosilicas were synthesized by two methods:

- with a combined high-temperature hydrolysis of $SiCl_4$ and $TiCl_4$ vapours – samples of a series TAS (Table 1);
- CVD method – by hydrolysis of $TiCl_4$ molecules chemisorbed on the surface of a highly dispersed silica – samples TS (Table 2).

In the study we also used the sample TAS-3_{mod} – titanosilica TAS-3 modified by octamethylcyclotetrasiloxane (OMCTS). This sample contained 15.5 μmol m^{-2} of grafted dimethylsilyl groups.

Table 1 Some properties of TAS titanosilicas

Oxides	TiO_2/mass%	S_{BET}/* m^2 g^{-1}	a_m/μmol m^{-2}
SiO_2	–	300	6.5
TAS-1	9	215	8.0
TAS-2	14	137	11.6
TAS-3	20	72	25.7
TAS-4	29	60	29.8
TAS-5	36	90	15.9
TiO_2	100	80	11.0

*Measurement of specific surface area has been carried out at –196°C using argon adsorption gas

Adsorption studies were carried out at 298 K in a vacuum sorption set-up with a McBain spring balance (sensitivity of balance is 1–3 mg mm^{-1}). Before adsorption measurement sorbents were evacuated 2 h at $p=10^{-1}$ Pa and temperature 673 K. Adsorptives were preliminarily freed of the dissolved air by a repeated freezing-thawing during evacuation.

Upon treatment of adsorption data we used ideas of the authors [6, 7] that, though the BET equation cannot describe the isotherm in the wide range of fillings of such chemically inhomogeneous surfaces, however, so far as in initial portions of isotherms the experimental points coincide well with the straight lines in coordinates of the BET equation, it can be evaluated constants of the equation, in particular, a capacity of monolayer (a_m). In spite of that absolute values of a_m have in a considerable extent a formal character, tendencies of their change allow to display features of adsorption process due to influence of the surface structure.

It was found that the adsorption of water on the surface of titanosilicas of a TAS series depends on a ratio silicon–titanium. The dependence of a sorption activity on composition has an extreme character: with increase in a content of TiO_2 in samples to

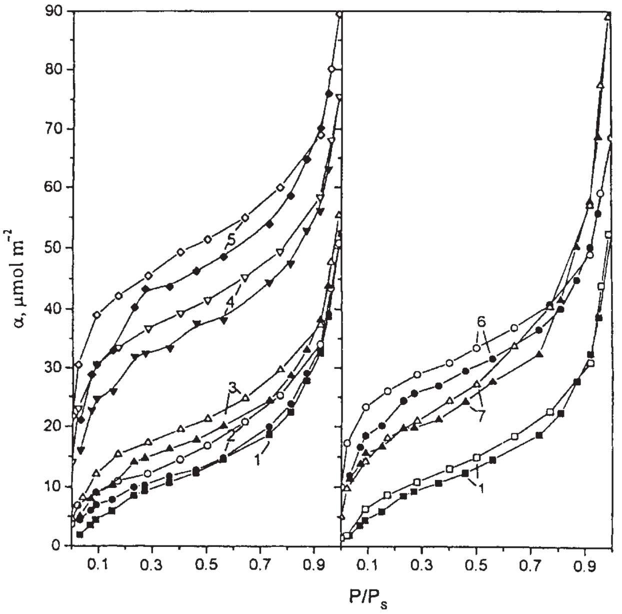

Fig. 1 Adsorption/desorption isotherms for water at 298 K on the samples: 1 – SiO_2; 2 – TAS-1; 3 – TAS-2; 4 – TAS-3; 5 – TAS-4; 6 – TAS-5; 7 – TiO_2. Solid symbol – adsorption, open symbol – desorption

29 mass%, a considerable increase of absolute isotherms of water adsorption in the whole range of relative pressures is observed, then a sorption activity of titanosilicas decreases (Fig. 1).

A quantitative estimate of adsorption properties of oxides being studied expressed in values of a monolayer capacity evidences that the maximum activity of the titanosilica surface (sample TAS-4) is about 4 times higher than that of the pure silica and 2 times than of the pyrogenic TiO_2 (Table 1).

Table 2 Some properties of TS samples

Oxides	TiO_2/mass%	Number of TiO_2 'layers'*	S_{BET}/m^2 g^{-1}	a_m,/mmol g^{-1}
SiO_2	–	–	269	1.54
TS-1	5.1	1.06	254	1.38
TS-2	9.6	2.00	273	1.40
TS-3	16.8	3.50	217	1.38
TS-4	22.2	4.62	187	1.25
TS-5	27.6	5.75	182	1.12
TS-6	33.0	6.87	154	1.14

*'Capacity of monolayer' of TiO_2 is 4.8 mass%

Adsorption of water vapours on samples of titanosilicas of the TS series is sharply different from the above given one. As follows from data of Table 2 with the increase of TiO_2 content in the sample the value of a_m decreases.

Previously, the use of IR-spectroscopy has showed [1, 8] that the main difference between titanosilicas of series TAS and TS produced by different methods is as follows. Primary particles of TAS samples consist of two phases of silicon and titanium oxides connected with titanosiloxane bridges, its number increases only to a definite content of TiO_2 – about 20%. Mixed TS oxides also consist of two phases of SiO_2 and TiO_2, however, titanosiloxane bonds are absent between them [9].

Titanosiloxane bonds are hydrolytically unstable and easily hydrolyze already at room temperature. The presence of hysteresis on adsorption isotherms covering a wide range of values of p/p_s (Fig. 1) indicates that a process of rehydroxylation runs on the surface of TAS samples [10]. In our opinion, namely the presence of titanosiloxane bonds on the surface of pyrogenic TAS is responsible for their increased activity in respect to water as compared to pure SiO_2, TiO_2 and titanosilicas synthesized according to CVD technology. Thus a dissociative adsorption of H_2O molecules on titanosiloxane bridges is accompanied by the appearance of new ≡SiOH and ≡TiOH groups which, in turn, become sites of adsorption of subsequent water molecules. It seems that a process of hydrolysis of titanosiloxane bonds is only limited by the near-surface layer since titanosilicas, though they contain hydrolytically unstable fragments, are quite stable to water. This fact is well consistent with the general tendency of a sharp increase in a hydrolytic stability of heterosiloxanes on a passage from linear structures to space ones [11].

Table 3 Adsorption properties of oxides in relation to water and alcohol molecules

Oxides	Capacity of monolayer, $a_m \cdot 10^4$/cm^3 m^{-2}		
	water	methanol	propanol-2
SiO_2	1.8	3.3	3.3
TiO_2	2.2	3.0	3.2
TAS-3	4.4	3.3	3.3
TAS-3_{mod}	3.9	1.8	1.4

Only water molecules seem to possess an ability to form new adsorption centers when breaking titanosiloxane bonds. In the case of its nearest analogs – methanol and propanol-2 it was noted that they are sorbed on the studied samples equally in fact. Table 3 gives values of a_m expressed in volume units which evidence that adsorption of given alcohols on the surface of the most active TAS and pure silicon and titanium oxides is practically equal. An equality of volumes of methanol and propanol-2 monolayers in all cases (except TAS-3_{mod}) allows the conclusion to be made that any significant disturbances of a structure in the phase interface of the pyrogenic titanosilica are absent, and adsorption of TAS relative to water is due to hydrolysis of Si–O–Ti bonds. In favour of this, also the circumstance evidences that the chemical modification of the surface with octamethylcyclotetrasiloxane influences a little adsorption of water with titanosilica (sample TAS-3_{mod}). As it is known, interaction of OMCTS with silicon or titanium oxides takes place by substitution of hydroxyl groups by dimethylsilyl, as a result, the surface becomes hydrophobic [12]. Therefore, a high adsorption activity of the TAS-3_{mod} sample relating to water characterizes the important part that titanosiloxane bonds play in this process.

Conclusions

Based on the results of studies, the conclusion has been made that properties of mixed oxides of silicon and titanium are determined not only by their chemical composition but also the way of production. It was established that the presence of hydrolytically unstable Si–O–Ti bonds on the surface of highly dispersed titanosilicas is responsible for their increased adsorption activity in relation to water molecules. A dissociative adsorption of H_2O on titanosiloxane bridges is accompanied by the appearance of additional groups of ≡SiOH and ≡TiOH, which, in turn, become adsorption sites for subsequent water molecules.

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