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Reaction of Diethyl Butane-1-phosphonate with the Surface of Tin Dioxide

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Abstract—Reaction of diethyl butane-1-phosphonate with the surface of tin dioxide was studied. The reaction involves grafting of the phosphonate residue onto the oxide surface; in the process, one or both ethoxy groups are eliminated. The resulting grafted layer exhibits fairly high resistance to hydrolysis and heat.

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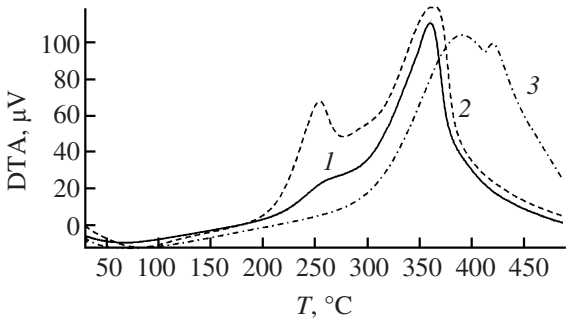
Chemical modification of the surface of dispersed and bulk mineral oxides allows preparation of a wide range of hybrid materials whose physical properties are determined by the support material, and chemical properties, by the nature of the covalently immobilized compound. The range of applications of surface-modified hybrid materials is extremely wide. Such materials are used as selective sorbents, heterogeneous catalysts, sensors, polymer fillers, etc. Chemically immobilized grafted molecular layers allow control of the adhesion and hydrophilic–lipophilic balance. They also exhibit corrosion-protective properties. Elucidation of regular trends in chemical modification is necessary for controlling the surface properties of a material in relation to a particular practical task. The best developed in this respect is the modification of silica surface. Dispersed silica is a convenient support for grafting of various functional groups. It has high specific surface area, it is stable, and can have diverse pore structures. At the same time, it is also necessary to develop procedures for chemical modification of the surface of other mineral oxides, such as oxides of tin, aluminum, copper, etc. Each of these oxides is of potential interest for chemical modification as a matrix having unique intrinsic properties.

An important application of tin dioxide is its use as material for electrodes and gas sensors. Chemical modification of the surface can enhance their sensitivity and selectivity. The uniqueness of tin dioxide as material for gas sensors is associated with its certain physicochemical properties. First, tin dioxide is a wide-band-gap *n*-type semiconductor. Therefore, the electrical conductivity of tin dioxide is extremely sensitive to the state of the surface just in the temperature range (300–800 K) characteristic of redox reactions on the oxide surface. Second, the surface of tin dioxide exhibits high adsorption properties and high reactivity, which is due to the presence of free electrons in the conduction band of tin dioxide and to the presence of surface and volume oxygen vacancies and of active chemisorbed oxygen.

Modification of tin dioxide with silanes has been reported [1, 2]. Nevertheless, such modifiers have certain drawbacks, one of which is that modifiers of this type do not eliminate nonuniformity of the tin dioxide surface associated with the presence of sorption centers of different types (as it occurs, e.g., in modification of aluminum oxide with phosphonates [3]). Therefore, modification of the tin dioxide surface with organophosphorus compounds is of appreciable interest.

Tin dioxide prepared as support in our study had the following characteristics:

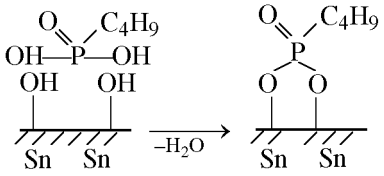
Matrix	S	O_2
Specific surface area S_{sp}, $m^2\ g^{-1}$		90
Total pore volume, $cm^3\ g^{-1}$	0.15	
Mesopore volume V_p, $ml\ g^{-1}$		0.07



Derivatograms of tin dioxide samples modified with diethyl butane-1-phosphonate: (*1*) traditional procedure, (*2*) impregnation at 120°C, and (*3*) impregnation at 200°C.

As seen from these data, the support has a well developed surface. The grafted layer on the surface of such supports can be relatively simply studied by standard procedures.

Today organophosphorus compounds such as phosphonic acids and their derivatives are among the most promising silicon-free modifiers. The scheme of their reaction with the support surface is shown below.



Phosphonic acids are known as modifiers of the oxide surface [9]. However, they often cause surface degradation. Therefore, as modifiers we used diethyl butane-1-phosphonate. Modification was performed by two procedures: from solution (traditional procedure) and by impregnation. Impregnation was performed at 120 and 200°C. The results of analysis of the modified oxide are given below.

Modifier	*n*-BuP(O)(OEt)$_2$, "traditional" method	*n*-BuP(O)(OEt)$_2$, impregnation at 110°C	*n*-BuP(O)(OEt)$_2$, impregnation at 200°C
Carbon content of sample, %	1.68	2.30	2.73
Grafting density, nm^{-2}	2.47	3.40	4.18

It can be seen that the highest grafting density is attained when using impregnation, i.e., this method is the most efficient.

Hydrolytic stability of grafted phosphonate residues. To evaluate the hydrolytic stability of the grafted phosphonate layer we took the sample impregnated at 200°C as it had the highest grafting density. Data on the hydrolytic stability of the grafted layer in this sample are given in Table 1. Data on the hydrolytic stability of tin dioxide modified with phenyltriethoxysilane (samples were previously prepared in our laboratory) are given in Table 2 for comparison.

It can be seen that the grafted phosphonate layer is considerably more stable in acid solution than the organosilicon layer. Howeber, in alkaline solutions both are unstable.

Thermal stability of grafted phosphonate layers. The derivatograms of the tin dioxide samples modified with diethyl butane-1-phosphonate are shown in the figure.

It can be seen that in an inert atmosphere the grafted layer is stable up to approximately 350°C, and at higher temperatures it rapidly degrades. An interest-ing feature of the samples obtained at low tempera-tures (110 and 120°C) is the presence in the derivato-gram of the second peak at 200–250°C (the peak at 70–100°C, present in all the derivatograms, is due to water desorption and is the only peak in the derivatogram of unmodified tin dioxide). Apparently, this peak may be associated with the elimination of the second ethoxy

Table 1. Hydrolytic stability of grafted phosphonate layer on the surface of tin dioxide, *n*-BuP(O)(OEt)$_2$ modifier

pH	Carbon content, %	Amount of grafted groups, nm^{-2}	Amount of grafted groups, % of initial content
–	2.30	3.4	
1	2.03	3.0	88
4	2.24	3.3	97
7	2.30	3.4	100
10	2.17	3.2	94
12	0.55	0.8	24

group from the modifier moiety, i.e., at these temperature the modification involves only one ethoxy group of diethyl butane-1-phosphonate. In the derivatogram of the sample prepared at 200°C this peak is virtually absent, which suggests elimination of both ethoxy groups of the modifier. Similar stepwise elimination of the methoxy groups in chemisorption of dimethyl methanephosphonate was observed previously [10].

EXPERIMENTAL

Initial Support. **Preparation of SnO_2 with a highly developed surface**. From anhydrous tin tetrachloride, we prepared a 1.7% aqueous solution. Then a 12% NH_4OH solution was added dropwise to pH 6–6.3.

$$SnCl_4 + 4NH^4OH \rightarrow SnO_2{\cdot}nH_2O\downarrow + 4NH_4Cl + 2H_2O,$$

$$SnO_2 \cdot nH_2O \xrightarrow{350^\circ C} \alpha\text{-}SnO_2 + nH_2O\uparrow.$$

The resulting α-stannic acid gel was washed with an aqueous solution of ammonium nitrate to remove chloride ions, dried at room temperature, and calcined at 350°C for 6 h.

The specific surface area of the support was determined by adsorption of nitrogen at a constant pressure on a vacuum adsorption unit.

Determination of the total pore volume (pipet method). A cone flask with a stopper was weighed, charged with tin dioxide powder, and weighed again. Then a liquid with a known density (water) was slowly added dropwise to the sorbent with vigorous shaking until the powder particles started to stick together and the resulting lumps no longer disintegrated on shaking. The stoppered flask was weighed again, and the volume of the liquid taken up, corresponding to the total pore volume [6], was determined.

The volume and mean size of micro- and mesopores were estimated by the desiccator method from adsorption of benzene.

Determination of the volume of micro- and mesopores (desiccator method). Weighing bottles were charged with 0.5–1-g portions of the dried samples. The samples were kept in an atmosphere of benzene vapor to constant weight.

The weight of benzene absorbed by the sample was determined from the difference between the weights of the sample saturated with benzene (M_1) and dry initial sample (M_0). The mesopore volume (V_p) was determined taking into account the benzene density (d^t_{benz}, $cm^3\ g^{-1}$):

$$V_p = (M_1 - M_0)/(d^t_{benz}M_0).$$

Then, knowing the specific surface area (S_{sp}), we determined the mean pore diameter (D_p, nm) [7]:

$$D_p = 4000V_p/S_{sp}.$$

Table 2. Hydrolytic stability of grafted organosilicon layer on the surface of tin dioxide, $PhSi(OEt)_3$ modifier

pH	Carbon content, %	Amount of grafted groups, nm^{-2}	Amount of grafted groups, % of initial content
–	1.70	1.6	
1	0.83	0.9	56
4	1.00	0.9	56
7	1.15	1.1	69
10	1.11	1.1	69
12	0.55	0.5	31

Synthesis of the Modifier (Diethyl Butane-1-Phosphonate). **Diethyl hydrogen phosphite** was prepared by the following scheme [6]:

$$3C_2H_5OH + PCl_3 \xrightarrow{0^\circ C} (C_2H_5O)_2P(O)H + 2HCl + C_2H_5Cl.$$

Ethanol was dried for 1 day over anhydrous copper sulfate, decanted, and distilled. 170.3 ml of thus dehydrated ethanol was transferred into a 250-ml two-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser. Phosphorus trichloride (87.5 ml) was slowly, added over a period of 1 h, from the dropping funnel to the flask cooled to 0°C. After adding the whole amount of PCl_3, the mixture was stirred for an additional 6 h, and the flask was connected to a water-jet pump to remove HCl from the mixture. The resulting diethyl hydrogen phosphite was distilled in a vacuum (100°C, 30 mm Hg). Yield 78%.

Alkylation of diethyl hydrogen phosphite followed the procedure described in [8]:

$$2\,(C_2H_5O)_2P(O)H + 2Na \rightarrow 2\,(C_2H_5O)_2P(O)Na + H_2,$$

$$C_4H_9X + (C_2H_5O)_2P(O)Na \rightarrow (C_2H_5O)_2P(O)C_4H_9 + NaX.$$

A 250-ml two-necked flask equipped with a magnetic stirrer and a reflux condenser was charged with 250 ml of anhydrous diethyl ether and 48 ml of diethyl hydrogen phosphite. Sodium metal (5.75 g) was gradually added. After sodium dissolved completely, a dropping funnel was attached to the flask and the calculated amount of 1-bromobutane (26 g) was gradually added. After adding the whole amount of the reagent the mixture was stirred for an additional 8 h. The resulting diethyl butane-1-phosphonate was distilled in a vacuum, bp 84°C (13 mm Hg). Yield 75%.

Modification of tin dioxide with diethyl butane-1-phosphonate. **Traditional method**. Modification of tin dioxide was performed in a three-necked flask equipped with a power-driven stirrer and a reflux condenser. The flask was charged with 1 g of the support and 100 ml of absolute toluene. The mixture was heated to reflux, and the modifier was added. The modifier was taken in an amount corresponding to the grafting density of 10 nm^{-2}. Then the powder was washed and dried by the standard procedure. **Impregnation method**. A round-bottom flask was charged with a weighted portion of tin dioxide. Then hexane was added in a volume equal to the double volume of tin dioxide. After that, the modifer was added in an amount corresponding to 50 modifier molecules per 1 nm^2 of the tin dioxide surface. The solvent was removed on a rotary evaporator, and the resulting powder was heated at 120°C for 24 h, after which it was washed and dried by the standard procedure. e*lemental analysis*. Elemental analysis of modified samples of tin dioxide was performed on a Carlo Erba device (Italy). The carbon content of the tin dioxide samples was determined by combustion of the substance in a fast oxygen stream, after Korshun and Klimova [9]. The amount of the modifier on the surface (nm^{-2}) was calculated by the formula

$$N = [(6.02\cdot10^5\cdot P_C)/(1200\,n_C - P_C M')](1/S_{sp}),$$

where P_C is the carbon content (%); n_C, amount of carbon atoms in the modifier molecule; S_{sp}, specific surface area of the support; M' (g mol^{-1}) = $M - nM_x + 17n - 18F$ (M' is the reduced molar weight of the modifier; M, molar weight of the modifier; M_x, molar weight of the leaving groups in the modifier molecule; F, mean number of bonds formed by the modifier molecule with the surface, equal to 1 for monofunctional silanes and 1.5 for bi- and trifunctional silanes [10]).

Evaluation of the hydrolytic stability of the modified supports. Tests were performed with aqueous solutions of H_2SO_4 (pH 1, 4), NaOH, and Na_2CO_3 (pH 7, 10, 12).

Two weighed portions (1 g) of the modified oxide were placed in test tubes, and each was charged with 10 ml of a solution with appropriate pH value. The test tubes were stoppered and allowed to stand for 24 h with intermittent shaking. Then the supernatant was decanted, and the powders were transferred with distilled water onto a filter and washed with distilled water (10×20 ml). The samples were dried in an oven at 110°C for 24 h.

Thermal studies were performed with a Netzsch STA 449 C device in an argon atmosphere. The temperature range was 20–500°C, and the heating rate, 10 deg min^{-1}.

REFERENCES

1. Moses, P.R., Wier, L.M., and Murray, R.W., *Anal. Chem.*, 1975, vol. 47, no. 12, p. 1882.
2. Untereker, D.F., Lennox, J.C., Wier, L.M., Moses, P.R., and Murray, R.W., J. Electroanal. Chem., 1977, vol. 81, p. 309.
3. Buchnev, M.V., Mingalev, P.G., Serdan, A.A., et al., *Zh. Anal. Khim*., 2003, vol. 58, no. 8, p. 838.
4. Mingalev, P.G. and Lisichkin, G.V., *Usp. Khim*., 2006, vol. 75, no. 6, p. 604.
5. Berger, F., Brunol, E., Planade, R., and Chambaudet, A., *Thin Solid Films*, 2003, vol. 436, p. 1.
6. Khokhlova, T.D., *Doctoral (Chem.) Dissertation,* Moscow: Mosk. Gos. Univ., 2001.
7. Kel'tsev, N.V., *Osnovy adsorbtsionnoi tekhniki* (Principles of Adsorption Technique), Moscow: Khimiya, 1984.
8. Kosolapoff, G.M., *J. Am. Chem. Soc*., 1945, vol. 67, no. 7, p. 1180.
9. Korshun, M.O. and Klimova, V.A., Osnovnye *mikrometody analiza organicheskikh* soedinenii (Main Methods of Organic Microanalysis), Moscow: Khimiya, 1978, p. 21.
10. *Modifitsirovannye kremnezemy v sorbtsii, katalize i khromatografii* (Modified Silicas in Sorption, Catalysis, and Chromatography), Lisichkin, G.V., Ed., Moscow: Khimiya, 1986.