Russian Chemical Reviews **75** (6) 541 – 557 (2006) © 2006 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2006v075n06ABEH002478

Chemical modification of oxide surfaces with organophosphorus(V) acids and their esters

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Abstract. Published data on modification of oxide materials with phosphonic and phosphinic acids and their derivatives are systematised and generalised. The regularities of formation of grafted modifier layers on the oxide surfaces are considered. It is shown that phosphonic acids and their derivatives can form dense well-ordered layers. The factors affecting the properties of such layers are analysed. The key applications of these modifiers are considered. The bibliography includes 146 references.

I. Introduction

Chemical modification of the surface of mineral supports is a commom method for fabrication of a broad spectrum of surface-modified materials, such as chemical and biological sensors, modified electrodes, separation membranes, selective adsorbents, sorbents for HPLC, heterogeneous metal complex catalysts, implants, antiadhesants, anticorrosion coatings, *etc*.[1] The most widely used materials are based on silica, which can be best chemically modified with organosilicon compounds.[2–5] However, at present the family of surface-modified materials has been considerably extended due to the use of other mineral supports (various oxides and metals) and some other modifiers. As a result, organosilicon compounds no longer play the role of universal modifiers.

Generally, the molecule of a modifier must contain three fragments (Fig. 1). These are a functional group that determines the chemical properties of the surface-modified material, an anchoring group responsible for immobilisation of the modifier molecule on the support surface through covalent bonding and a spacer (or linker) that connects the functional group to the anchoring group, thus completing the structure of the modifier molecule.

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Received 8 June 2005
Uspekhi Khimii **75** (6) 604 – 624 (2006); translated by A M Raevskiy

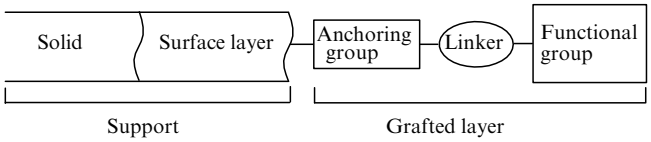


Figure 1. Structure of the surface of a chemically modified support.

Modification of the surface of oxide materials usually involves electrophilic substitution (a surface hydroxyl proton is replaced by the anchoring group of the modifier). From this it follows that the modifier molecule must contain a leaving group that forms a stable compound with proton.

The requirements for the anchoring group are as follows: the anchoring fragment should have a valence of at least two, because otherwise it cannot be bound to the surface; the reaction between the groups present on the support surface and the anchoring group should follow an unambiguous pathway and proceed as fast as possible; and the system of chemical bonds between the support and the grafted layer should be stable under the operational and storage conditions of the surface-modified material. It is also desired that the modifier be non-toxic † and the synthesis of this compound be not too complicated. Most often, silicon and phosphorus are used as the anchoring elements. Other anchoring elements include B, C, N, S, Ge, As, Sn, Sb, Hg and Pb.

The surface of silica is usually modified with silicon anchoring groups SiX_n because they meet the requirements mentioned above. The interaction of these groups with the surface hydroxyl groups of silica results in the formation of a hydrolytically stable system of chemical bonds Si–O–Si–C. The next in use are organophosphorus compounds to which this review is devoted. In order to provide strong bonds with the surface OH groups of oxide materials, the anchoring phosphorus atom in organophosphorus compounds should be bound to such reactive groups, as OH, OR or Hal; *i.e*., the modifier molecule should be an organic phosphorus acid or its derivative. Trivalent phosphorus acids (phosphonous and phosphinous acids) are oxidised in air, which

† The use of alkyl compounds of tin or mercury as surface modifiers is permissible, but special care should be taken.

makes them undesired as modifiers because the properties of the grafted layer of a sample exposed to atmosphere will change with time in an uncontrollable and unpredictable manner. From this it follows that the most appropriate organophosphorus modifiers of oxide surfaces are phosphorus(V) acids (phosphonic and phosphinic acids) and their derivatives.

II. Modification of silica and mica surfaces

At present, 60% to 80% of all surface-modified materials are based on silica. This is due to considerable advantages of this material and first of all, to the possibility of varying its structural characteristics (specific surface area, pore diameter and volume, and particle shape and size) over a wide range. A great advantage of silica is also its low catalytic activity, which appreciably decreases the probability of undesired side reactions. Silicas are also well studied, readily available and cheap. Modification of silica with organosilicon compounds has long been known and well studied (see, *e.g.*, Refs 1, 2) and we will not dwell on it. Our attention will be focussed on the modification of silica with phosphonic acids.

The interaction of phosphonic acids with silica has been documented.[6–10] When silica is refluxed with phosphonic acids for 2 h in chlorobenzene, a signal appears in the ^{31}P NMR spectra, which differs from the signal of the acid adsorbed on silica and remains after washing the support with n-propanol and propan-2-ol. The signal was attributed [6] to phosphonate groups formed on the silica surface. This is quite surprising because phosphonic acids do not undergo esterification (with, *e.g.*, ethanol) on reflux. The authorsassumed that the interaction of phosphonic acids with the silica surface involves the formation of an intermediate containing a pentacoordinate silicon atom (here, the role of Lewis acid site is played by the silicon atom).

Boiling silica with *tert*-butylphosphonic acid in toluene results in grafting of the acid to the surface.[8] The grafting density is 1.5 nm^{-2} (from this point on the term 'grafting density' means the number of molecules per nm^2 of the surface area). The granulometric composition of the support remained unchanged after modification. The grafted layer is hydrolytically stable in a neutral medium (the grafting density decreases by 15% after storage of the modified samples in distilled water for 2 days at room temperature); however, its stability in acidic and alkaline media is much lower.[9]

The interaction of silica with methylphosphonic and phenylphosphonic acids was studied (Ref. 10). ^{31}P NMR experiments revealed the formation of a system of P–O–Si bonds on the silica surface.

Phosphonic acids interact with the silica surface much less readily than with the surfaces of most metal oxides. It was reported that long-chain phosphonic acids do not interact with the silica surface at all [7] and that dialkyl esters of phosphonic acids behave analogously.[9, 10] Nevertheless, slow decomposition of dimethyl methylphosphonate into methanol and methyl methylphosphonate on hydroxylated silica under severe conditions is possible.[11] Methyl methylphosphonate can be partially grafted on the surface, however the grafting density is very low even under such conditions. Dexydroxylated silica does not interact with dimethyl methylphosphonate.[11]

The surface of silica was modified by dichloroanhydride of butylphosphonic acid and by dibutylphosphinic acid.[9] The grafting density was $\sim$1 nm^{-2} in both cases. The hydrolytic stability of the layers prepared was low, being similar to that of the layers formed in the modification of silica with phosphonic acids.[9]

Considerable attention is paid to chemical modification of the surface of mica crystals. Mica is a convenient object for wetting studies and for atomic force microscopy (AFM) studies of the surface, because its crystals can be broken with ease into smaller pieces with extended smooth facets. The facet surfaces contain oxygen–silicon tetrahedra and are very similar to the silica surface. It should be noted that the surface of a perfect facet of a mica crystal contains only siloxane groups, and a real facet can contain defects (silanol groups).[12, 13]

Octadecylphosphonic acid does not form a dense monolayer on the mica surface.[14] Modification of the surface of a fresh facet on a mica crystal with octadecylphosphonic acid by melting followed by heating at 130 °C for 2 h leads to incomplete coverage of the mica surface.Besides, the modified regions can be multiply covered (additional octadecylphosphonic acid molecules are attached to the surface through van der Waals interactions with neighbouring molecules). Similarly to clean mica surface, non-modified areas are highly hydrophilic,‡ whereas modified regions are hydrophobic and non-hygroscopic.

Treatment of mica facets with a solution of octadecylphosphonic acid in tetrahydrofuran results in the formation of self-assembled monolayers comprised of the acid molecules on the mica surface.[15] An AFM study of the samples characterised by different modification time revealed the formation of 'islands' of strongly grafted molecules on the surface (surface coverage of about 25%) after 1 min of treatment, which begin to grow and merge, thus producing a dense monolayer. Only small surface defects (surface coverage of about 85%) remain unmodified after 30 min while after 120 min the surface becomes almost uniformly covered (surface coverage of about 95%).

Octadecylphosphonic acid forms round 'islands' on the mica surface in contrast to octadecyltrichlorosilane 'islands' that have a fractal morphology [16] due to qualitatively different mechanisms of grafting of these compounds. Octadecyltrichlorosilane rapidly and almost irreversibly reacts with the mica surface and forms strong covalent bonds with surface hydroxyl groups and neighbouring modifier molecules. The modifier molecules are grafted at the positions where the anchoring groups contact the support surface. This leads to diffusion-controlled aggregation and fractal morphology of 'islands' thus formed. The octadecylphosphonic acid molecules are not linked to one another and interact with the silica surface slowly and (to a great extent) reversibly. This allows them to be involved in some kind of lateral diffusion and, as a consequence, makes possible molecular rearrangements within the grafted layer. The fact that most 'islands' are round suggests linear tension (analogue of surface tension for two-dimensional case) at the 'island' – bare surface interface. It should be noted that although the grafted layer formed after treatment of the surface with octadecylphosphonic acid is highly ordered, the alkyl chains are characterised by rather loose packing. Namely, each molecule occupies a surface area of nearly 0.25 nm^2 while the angle between the alkyl chains and the normal to the surface (tilt angle) is 40°. It is interesting that even at the shortest modification times (less than 1 min) the surface coverage is rather high (about 25%).

Contact angle measurements for the mica crystal surfaces modified with octadecylphosphonic acid [15] revealed the following regularities. The cosine of the contact angle of the hexadecane on modified surface is a linear function of the surface coverage with the modifier molecules. The contact angle changes from 20° for bare mica crystal to 45° for the fully modified crystal. The contact angle on fully modified surface compares well with that obtained for well-formed thiolate monolayers, which indicates a high degree of ordering of the monolayer.

The cosine of the contact angle of water on the modified mica surface linearly decreases only to nearly 50% coverage and then reaches a maximum value.§ The contact angle of water on bare mica surface is 3°.

The inflow and outflow contact angles were also determined, the former being about 5° larger than the static contact angle while the latter being very small ($< 10°$). It should be noted that the contact angles of water on the mica surface decrease with time. This can be due to hydrolytic instability of layers formed.

‡ In air, a water film up to a nanometre thick is formed on these areas.
§ The maximum attainable contact angle for the monolayers under study is 90°.

An AFM study [17] of *in situ* growth of octadecylphosphonate 'islands' on mica in tetrahydrofuran confirmed the conclusions made earlier.[15] Namely, modification of the mica surface begins with nucleation followed by growth of 'islands' which then merge into a monolayer. No motions of 'islands' relative to one another were observed in the course of modification. It is likely that a proportion of octadecylphosphonic acid molecules is aggregated in solution; these aggregates grafted in the surface serve as nuclei. The growth of 'islands' is consistent with an accretion model, according to which disordered acid molecules present on bare mica surface (they cannot be detected by AFM) gradually diffuse towards an 'island', thus making its growth possible. Bubbling air through the solution led to a jumpwise increase in the surface coverage. This is due to the presence of octadecylphosphonic acid monolayer at the solution–air interface.[17] To check this assumption, experiments involving multiple short-term (less than 1 s) dips of samples into the modifier solution. It was found that the surface coverage increases with the number of dips and the fraction of a monolayer per dip increases in proportion to the octadecylphosphonic acid concentration in the solution. This substantiates the assumption made above.

A comparative analysis of the growth of octadecylphosphonic acid monolayers on sapphire and mica surfaces was reported.[18] It was found that mica is less reactive than sapphire. At room temperature, a monolayer providing a water contact angle of 90° is formed after 1 min on sapphire (from 5×10^{-5} M solution) and after several hours on mica. Octadecylphosphonic acid layers on sapphire are more ordered than on mica, namely, at room temperature the acid forms a highly ordered quasi-crystalline layer on sapphire while disordered liquid-expanded layers are formed under identical conditions on mica.

The thermal stability of grafted phosphonic acid layers is almost independent of the nature of support.[19]

III. Modification of alumina surface

Following silica, alumina is the next in significance among oxide supports used in the synthesis of surface-modified materials. As silica, alumina is relatively cheap and available. Significant drawbacks of Al_2O_3 compared to SiO_2 are a nonuniform surface and the dependence of the surface properties on the sample prehistory. Additionally, the presence of strong Brønsted or Lewis acid sites on the Al_2O_3 surface can cause undesired transformation of the modifier molecules. At the same time alumina offers certain advantages over silica, *e.g.*, higher mechanical stability and greater stability in alkaline media.

The importance of studies on the regularities of modification of Al_2O_3 surface is first of all determined by the fact that such valuable material as metallic aluminium is always covered with oxide film.

Phosphonic acids offer considerable advantages over organosilicon compounds in the modification of Al_2O_3 surface. This is first of all due to the presence of strong acid sites on the Al_2O_3 surface, which significantly facilitates the donor–acceptor interaction of phosphoryl group of the modifier with the Lewis acid sites (unoccupied sites or those formed from a proportion of Brønsted sites due to competitive displacement of other nucleophilic groups). This interaction makes the phosphorus atom more electrophilic and facilitates a subsequent reaction between the modifier and the surface hydroxyl groups. Besides, this donor–acceptor interaction helps the anchoring groups of the modifier molecules to block efficiently the surface acid sites, so the surface becomes more uniform and non-specific.

Conventional organosilicon modifiers (*e.g.*, ethoxysilanes) do not readily react with the alumina surface (see, *e.g.*, Ref. 20). High grafting density can be reached only with silanes that contain two or three leaving groups at silicon atom and can therefore form horizontal cross-links with neighbouring modifier molecules. The use of chlorosilanes for modification of alumina is complicated by the fact that hydrogen chloride evolved in the reaction causes destruction of Al_2O_3 surface and uncontrollable changes in the structural and geometric parameters of the support and the surface acidity. The addition to the reaction mixture of a compound that can react with hydrogen chloride (*e.g.*, organic amine) leaves the situation unchanged, because this component is sorbed on specific (acid) surface sites and also causes uncontrollable changes in the properties of the modified support thus formed. It seems likely that good results would be obtained with silicon hydrides as modifiers; however, the interaction of these compounds with Al_2O_3 surface has been poorly studied. Additionally, such compounds (especially those having small substituents at silicon atom) are less available and less stable than chloro- and alkoxysilanes. Therefore, it is not surprising that most studies on the modification of Al_2O_3 surface were carried out using phosphonic acids or their derivatives as modifiers.

1. Phosphonic acids

Phosphonic acids are one of three classes of compounds (in addition to thiols and trifunctional silanes) capable of forming dense self-assembled monolayers on support surfaces. Therefore, a large number of studies on the modification of Al_2O_3 surface are concerned with phosphonic acids. It should be noted that a self-assembled monolayer is the best grafted layer, because it provides the highest extent of screening of the support surface.

Self-assembled monolayers comprised of *n*-octadecylphosphonic acid molecules on the (1000) and ($1\bar{1}02$) faces (C- and R-faces, respectively) of a sapphire single crystal were studied by AFM, contact angle measurements and FTIR spectroscopy.[18] It was established that the formation of monolayer strongly depends on temperature. This was explained by a three-phase model for film deposition. At low temperature, close-packed molecular 'islands' nucleate and grow on almost bare substrate surface (two-dimensional transition vapour–solid),¶ while at high temperature two-dimensional transition liquid–solid occurs and a film is formed on the surface.

A change in the contact angle in the surface modification implies the formation of a surface film, however AFM measurements failed to detect it. As the modification time increases, structures with poorly defined boundaries appear on the surface, which can be detected by AFM. These structures become larger as the treatment duration increases. The height of the structures (0.8 nm for the C-face and ~0.55 nm for the R-face) does not reach a value consistent with a fully extended octadecylphosphonic acid molecule (~2.5 nm). The water contact angle on the sapphire surface treated with octadecylphosphonic acid (1 min) is 90° and remains unchanged upon increase in the modification time. However, treatment of sapphire surface with n-hexadecylphosphonic acid for 1 min results in the formation of a layer for which the water contact angle is 31°; the contact angle increases to 36° as the treatment time increases to 0.5 h for the C-face and to 1 h for the R-face.

At low temperatures, the growth of a surface modifier layer is significantly different from that described above. At 2 °C, small 'islands' with well-defined boundaries are formed. The height of the 'islands' is about 1.1 nm. The surface coverage increases with time, but slowly, and the surface remains incompletely covered even after treatment for 15.5 h.

A FTIR study of the modified sapphire surface showed that treatment of the surface for 1 min at room temperature is followed by the formation of disordered ('liquid-expanded') layers, which become much more ordered after 1 h. Modification at 2 °C leads to the formation of highly ordered layers. The results obtained suggest a two-dimensional phase diagram for the grafted layer (in

¶ Two-dimensional transition means that molecules are transferred over a surface. In this case highly ordered close-packed regions of the grafted layer are treated as solid, disordered close-packed regions are treated as liquid and regions with a grafting density much lower than that characteristic of the monolayer are treated as vapour.

the 'temperature – grafting density' coordinates). The 'liquid-expanded' disordered state of the grafted layer in this system is only possible at temperatures above 11 °C. This temperature corresponds to a triple point.

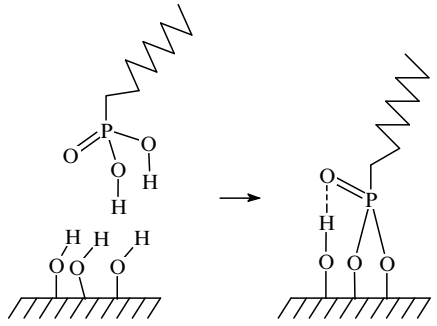
The kinetics of growth of the modifier layer on the C- and R-sapphire faces are different. Namely, the growth rate on the C-face is higher and the growing layer is thicker; this is due to different surface enenrgies of these faces. The R-face is formed by a layer of oxygen atoms while the C-face is formed by a layer of aluminium atoms (the surface area of the C-face is smaller than that of the R-face); the C-face contains a larger number of coordinatively unsaturated sites and is characterised by higher surface energy. Assuming epitaxial growth of a modifier layer, it is clear that the layer growing on the C-face will be thicker. The modification temperature can be shifted towards high-temperature region owing to proximity to the face edge or other surface defects. Generally, by varying the temperature it is possible to control the amount of defects within the grafted layer.

Self-assembled monolayers comprising the molecules of three phosphonic acids, namely, $CF_3(CF_2)_7(CH_2)_{11}PO_3H_2$,† n-$C_{16}H_{33}PO_3H_2$ and n-$C_{22}H_{45}PO_3H_2$ on the surface of aluminium covered with native oxide film were studied by IR spectroscopy, ellipsometry and contact angle measurements.[21] It was shown that the layers formed by these three acids are characterised by significantly different structures and growth kinetics. For instance, the lack of ordering was observed for fluorinated phosphonic acid in all cases (layer becomes insignificantly more ordered with an increase in the modification time) while the layer thickness increases with time (from 1.8 nm after modification for 5 s to 2.3 nm after 24 h).

It should be noted that the behaviour of partially fluorinated phosphonic acids on the surface of oxidised aluminium is basically different from that of perfluorothiols on silver and gold surfaces.[22–24] This was explained by two factors, namely, larger size of the anchoring group PO_3H_2 compared to the thiol group and low lateral mobility of phosphonate groups on Al_2O_3 surface compared to that of thiol group on the noble metal surfaces.[21]

At long treatment times, the acids n-$C_{16}H_{33}PO_3H_2$ and n-$C_{22}H_{45}PO_3H_2$ form ordered layers in which alkyl chains are in fully transoid conformation. Different behaviour of these acids and the partially fluorinated acid is due to the presence of a bulky, conformationally rigid perfluorinated segment in the last-mentioned molecule; this precludes the close packing of alkyl groups. Additionally, some contributions from low solubility of the partially fluorinated acid in ethanol (solvent for modification) and micellisation in solution (although the authors reported no unambiguous proofs of micellisation) are also possible.

The IR spectra of the samples modified with these three acids exhibit no AlOH bands, which is associated with the interaction of these groups with OH groups of phosphonic acid molecules accompanied by the formation of a surface alumophosphonate layer.



† Acid $CF_3(CF_2)_7(CH_2)_{11}PO_3H_2$ forms on Al_2O_3 surface a grafted layer characterised by minimum surface energy.

The modification of Al_2O_3 surface with fluorinated phosphonic acid approaches its equilibrium rapidly. This acid forms disordered 'islands' on the surface, which then merge. The formation of a monolayer takes ~5–10 min. A considerable increase in the water contact angle for the modified surface is observed after modification over a period of 5 s. Docosylphosphonic acid n-$C_{22}H_{45}PO_3H$ also modifies the surface following the 'island' mechanism; however, alkyl chains in the 'islands' formed are ordered. In this case the kinetics of modification is similar to that of fluorinated acid. At the same time hexadecylphosphonic acid n-$C_{16}H_{33}PO_3H$ initially forms a disordered 'liquid-like' layer on the aluminium surface, which becomes more ordered as the modification time increases. In this case the equilibrium is attained after about 4 h. (An increase in the rate of formation of self-assembled monolayers in the presence of fluorinated modifiers was also detected in the case of fluoro derivatives of trichlorosilanes [25,26] and thiols.[27])

Contact angle measurements showed that water spills over the starting oxidised aluminium plates (contact angle equals zero). Surface modification imparts highly hydrophobic properties to the surface, that is, the contact angle for the surface modified with hexadecylphosphonic and docosylphosphonic acids is 110° (*cf.* 122° for partially fluorinated acid).

At low degree of modification, all modifier molecules are tridentate, *i.e.*, they form three covalent bonds with the oxidised aluminium surface. One of them is a donor-acceptor bond between the phosphoryl oxygen and the Lewis acid surface site).[21] As the modification time increases, bidentate and even monodentate modifier molecules appear on the surface. This is confirmed by the fact that for the tridentate molecules in the transoid conformation of alkyl chains within the grafted layer the tilt angle should be 35°. The films studied at high degrees of modification are characterised by much larger angles that increase with increasing the modification time.

A theory developed by the authors of Ref. 28 treats the surface layers as gas-like, liquid-like and crystal-like ones (layers can also be represented using a two-dimensional state diagram). The triple point of the layer comprising docosylphosphonic acid molecules is much higher than room temperature while that of a layer comprised of hexadecylphosphonic acid molecules is near room temperature. The triple point of the fluorinated acid and the crystalline-like state of the grafted layer are apparently inaccessible. Efforts were made in order to reach the crystal-like state for a fluorinated acid film by heating the modified sample followed by cooling, however heating to moderate temperatures (at most 250 °C) left the structure of the grafted layer unchanged, whereas heating above 250 °C led to irreversible destruction of the grafted layer.

Adsorption and self-assembly of phosphonic acids on oxidised surfaces of metallic aluminium were studied by X-ray photoelectron spectroscopy, Auger spectroscopy and FTIR spectroscopy.[29] The surfaces of high-purity aluminium (99.999%) and an industrial alloy containing 98.87% of aluminium, 0.76% of magnesium, 0.29% iron and 0.08% silicon were modified. Prior to modification, the samples were thoroughly polished. As a result, the surface of bare aluminium was optically smooth while iron inclusions were seen on the alloy surface. It was shown that self-assembly of layers is possible on both types of surfaces. Full coverage of the bare aluminium and alloy surfaces was reached after 100 s. Studies of the alloy samples characterised by shorter modification time showed that adsorption of phosphonic acids first of all occurs on iron inclusions and then on the aluminium surface. Magnesium and silicon impurities do not affect the formation of the grafted layer.

A packing study of alkyl chains in the grafted layer revealed initial formation of disordered layers followed by gradual ordering with an increase in the modification time. The formation of fully ordered grafted layers takes about 70 h.[29] The tilt angle of alkyl chains was determined from IR spectroscopy data.[30,31] Its value (31°) is similar to the corresponding angle for alkyl chains in

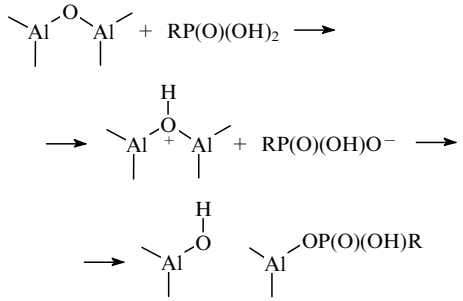
phosphonic acid bound to the surface in a tridentate fashion (35°). The somewhat lower magnitude of tilt angle may indicate the presence of coordinated groups of lower denticity on the surface. Unfortunately, the authors[29] did not report which alkylphosphonic acids were used for modification. This complicates the understanding of the results obtained.

Decylphosphonic acid can form films on the surfaces of bare aluminium and aluminium alloy 2024T3 containing inclusion phases of Al_7Cu_2Fe of size up to a few micrometres. The structure of such films was studied by X-ray photoelectron spectroscopy.[32] Prior to modification the samples were thoroughly polished and the oxide film was removed by bombarding them with argon ions. Immediately prior to modification the samples were exposed to air for a short time, which led to formation of a a thin surface oxide layer.

X-Ray photoelectron spectra showed that the oxide layer on the alloy surfaces contain small amounts of copper. P(2s) X-ray photoelectron spectroscopy data revealed a uniform coverage of the aluminium and aluminium alloy surfaces with decylphosphonic acid molecules and the absence of preferred or reduced sorption of the modifier on inclusions. At the same time the contact angle for the modified bare aluminium sample was 110°, being only 97° for the alloy, which indicates a lesser ordering of the grafted layer on the alloy surface. The reason for this is to be clarified.

The influence of preliminary long-term exposure of samples to air, nature of solvent and random sorption of hydrocarbon contaminations on sample surface on the quality of coatings were also studied.[32, 33]

The interaction of alumina with phosphonic acids is often accompanied by the formation of a surface aluminium phosphonate phase.[34]



For instance, a phosphonate phase is formed in the course of adsorption of phenylphosphonic acid from water at pH 4 and during treatment of alumina with bis(trimethylsilyl) phenyl phosphonate. However, the phosphonate phase was not detected when the modification was performed at pH 6 .

An attempt to prepare a monolayer coating by treating Al_2O_3 surface with octadecylphosphonic acid was reported.[7] However, breakdown of particles of the starting oxide and formation of only bulk phase of aluminium phosphonate were observed under the experimental conditions.

Adsorption of a range of organic molecules on the surface of magnetron-sputtered aluminium was studied.[35] Prior to modification the aluminium surface was exposed to air for a short time, which resulted in the formation of a thin oxide layer. Alkylphosphonic and alkanecarboxylic acids and aliphatic triethoxysilanes, trichlorosilanes, amines and epoxides were used as surface modifiers. The modification was carried out in toluene. It was found that phosphonic and carboxylic acids form well-ordered layers with the grafting density of about 5 nm^{-2} on aluminium surface, whereas trichlorosilanes form polymeric layers and other compounds form disordered layers with low grafting density. Under the experimental conditions, trichlorosilanes can destroy the aluminium surface and, in the limiting case, dissolve the sample. One can assume that this is due to hydrolysis of silanes with trace amounts of water present on the metal surface and in solvent (toluene).

Polarisation modulated IR reflection spectra revealed a low proportion of *gauche*-defects within the layers formed by phosphonic and carboxylic acids and a small tilt angle. Water contact angle measurements for acid treated aluminium surface showed that the contact angle remains unchanged after modification for 4–6 h in the case of carboxylic acids and after only 0.5 h in the case of phosphonic acids. The maximum contact angle values attained in these experiments were 120° for phosphonic acids and 117° for carboxylic acids. The water contact angles for surfaces of copper, silver and gold, modified with alkanethiols are 115°, 116° and 120°, respectively.[36] Taking into account that alkanethiols form highly ordered layers on the surfaces of these metals, one can consider that the layers formed by carboxylic and, especially, phosphonic acids are well-ordered. This is in good agreement with the published data [37] obtained for monolayer coatings formed by alkylphosphonic and alkylsulfonic acids.

The longer the alkyl group in the modifier molecule the larger the contact angle.[37–39] At the same time, sessile drop measurements of the contact angle provide information on the state of the modifier layer at a depth of at most four methylene units.[40] From this it follows that the effect mentioned above can be explained only by an increase in the degree of ordering of the grafted layer with elongation of the alkyl chain.

Higher density and ordering of the grafted layers of phosphonic acids compared to those of carboxylic acids are due to the ability of phosphonic acids to displace contaminants from the support surface. According to X-ray photoelectron spectroscopy data, the aluminium surface is always covered with carbonaceous contaminants. One can assume that they block the adsorption sites suitable for grafting. It was established that undecanoic acid is incapable of displacing all contaminants from aluminium surface, whereas decylphosphonic acid does it. This is apparently a reason for the higher degree of ordering of the grafted layer. Higher ability of phosphonic acids to displace contaminants from the support surfaces compared to carboxylic acids is likely due to greater stability of the tridentate anchoring group compared to bidentate carboxyl group.‡

A methodology for the formation and derivatisation of self-assembled monolayers of α,ω-alkanediyl-diphosphonic acids on conventional engineering metals, such as soft and stainless steels, aluminium, copper and brass was reported.[41] Diacids with different number of methylene units [$(CH_2)_{2n}$, $n = 1-6$] between phosphonic groups were studied. The surface modification was carried out in ethanol at room temperature and the treatment time was 15–30 min. Prior to modification, 1 equiv. of sodium hydroxide was added to the diphosphonic acid solution in order to bind only one phosphonate group to the surface and to leave the second acid group in the solution. The degree of ordering of monolayers formed increased with an increase in the length of the polymethylene chain. For instance, short-chain acids formed disordered surface layers while dodecyldiphosphonic acid formed highly ordered layers. Modification of steel surface in ethanol led to the formation of monolayers while the process in water mainly lead to formation of polylayers. The nature of this phenomenon is still unclear.

Further modification of diphosphonic acid monolayers involved complexation of free phosphonate groups with Zn^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, ZrO^{2+}, VO^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} and Ce^{3+} cations. Layers thus modified could participate in complexation with organic acids and polymers containing acid groups. The cations served as linkers connecting the phosphonate groups of the grafted layer to carboxylate or phosphonate groups of the 'incoming' acids. The thermal stability of such layers is rather high. For instance, thermal decomposition of a layer

‡ The ability to displace contamination from sorption sites is governed by the energy of the bond between the displacing group and the surface (other conditions being equal, the higher the denticity the higher the bond energy).

formed by a diphosphonic acid in the presence of Zn^{2+} cation linker in air begins at 250 °C. When the process is completed, a phosphate phase was left on the surface.

The action of a copolymer of ethylene and methacrylic acid on diphosphonic acid monolayer films results in a very strong composite. Composites based on long-chain diphosphonic acids efficiently inhibit metal corrosion in 5% hydrochloric acid, whereas composites based on short-chain diphosphonic acids exhibit no protective effect; moreover, in some cases corrosion of metal surfaces is enhanced.§

It should be noted that metal-modified monolayers possess a surprisingly high stability against organic acids. In particular, complexation of such layers with such a strong acid as perfluorooctanoic acid did not lead to destruction of the grafted layer.

Thermal stability and stability in various solvents (in particular, water) are important parameters of grafted layers. They determine the possibility of using grafted layers in liquid and gas chromatography, in catalysis, for corrosion protection, *etc*.

The dependence of the grafting density of alkylphosphonic acids on γ-Al_2O_3 surface on the structure of alkyl group and on the amount of the modifier employed was studied.[8] It was shown that alkylphosphonic acids readily interact with the oxide surface. In all cases the granulometric composition of oxide particles changed significantly, namely, relatively large oxide particles (100 – 200 μm) were transformed into small particles at most 2 μm in diameter. This is due to the fact that the interaction of alkylphosphonic acids with Al_2O_3 is not stopped at the stage of monolayer formation (grafting). The grafted phosphonic groups interact with the surface AlOH fragments to give aluminium phosphonate and the starting particles are destroyed, which is confirmed by high content of carbon in the samples obtained.

The dependence of the grafting density on the amount of modifier is strongly different for normal and branched alkyl groups. For instance, for *tert*-butylphosphonic acid the maximum grafting density is $\sim$2.5 nm^{-2} and remains almost unchanged as the content of the modifier in the reaction mixture increases. In the case of isopropylphosphonic acid the grafting density slightly increases with an increase in the modifier concentration, whereas for n-butylphosphonic acid the grafting density increases to almost complete consumption of modifier in the reaction mixture.

A study[8] of the hydrolytic stability of the grafted layers obtained showed that it is maximum, but not too high, in the range of neutral pH values (grafting density of the samples stored for 2 days in an aqueous medium at room temperature decreased by about 15%), being even lower in acid and alkaline media. The pore volume in the modified support was studied in relation to the type of the modifier and to the modification conditions. In most cases, modification strongly affects the pore volume in the support.

A thermogravimetric study of thermal stability of phosphonic acid monolayers on alumina surface was reported.[19] The modified samples exposed to nitrogen atmosphere showed a dramatic mass loss in the temperature interval 200 – 600 °C due to degradation of the grafted layer. Interestingly, the degradation onset temperature (200 – 250 °C) and the maximum mass loss temperature (400 – 450 °C) depend only slightly on the support nature. The activation energy of the degradation process (265±15 kJ mol^{-1} for the samples under study) behaves analogously. According to IR spectroscopy and elemental analysis data, after degradation of the grafted layer the support surface is covered with small amounts of carbon (mainly in the form of carbides) and the total phosphorus (as phosphates). It is significant that the grafted layers in air remain almost as stable as in inert atmosphere; the only exception is a decrease in the maximum mass loss temperature by 50 – 100 °C.

The thermal stabilities of layers of phosphonic acids, alkylsilanes ($RSiH_3$) and alkyldimethylchlorosilanes supported on Al_2O_3 surfaces were compared.[19] The thermal stability of the $RSiH_3$ layers is similar to that of the phosphonic acid layers while alkyldimethylchlorosilane layers are much less stable.

A computer simulation study of the reaction of vinylphosphonic acid with the (0001) face of alumina and its energy characteristics was reported.[42] In this system the acid molecules are attached to the support surface in a tripodal fashion.[43,44] Because of this, three types of sorption sites capable of interacting in such a manner were studied.[42] They differed in distances between adjacent hydroxyl groups and between the aluminium ion lying below the surface and the phosphorus atom. Additionally, bi- and monodentate interactions of vinylphosphonic acid with the surface were also simulated.

According to calculations, the binding enthalpy of vinylphosphonic acid depends on the geometry of the sorption site and on the distance from the phosphorus atom to the aluminium ion located under the surface plane. It was found that tripodal binding is characterised by the largest negative enthalpy, while monodentate binding by the smallest negative enthalpy. The arrangement of the vinyl fragment relative to the tridentate anchoring group has no effect on the enthalpy of reaction. The Al – O – P bonds that anchor the modifier molecule on the support surface are mainly ionic, with a small contribution of covalent bonding.

2. Phosphonates

Compared to phosphonic acids, phosphonates are much more rarely used for the modification of alumina. There are only a few studies on surface modification using this class of compounds. In particular, a study[34] on the modification of alumina with diethyl phenylphosphonate revealed the formation of monolayer diethyl phenylphosphonate film on the surface and the lack of bulk phase of aluminium phosphonate.¶ The modification of γ-Al_2O_3 surface with diethyl n-butylphosphonate also ceases at the stage of monolayer formation; no bulk phase of aluminium phosphonate was also observed. However, the grafting density attained under these conditions was low ($\sim$0.9 nm^{-2}).

The authors of a gas chromatographic study[45] of γ-Al_2O_3 surface modified with diethyl n-butylphosphonate reported a procedure for fabrication of coatings with high coverage (3.4 nm^{-2}, or about 70% of monolayer). The modified sorbents are significantly different from the starting Al_2O_3 and from alumina coated with squalane (20 mass %), being similar in properties to silica. This was attributed to the effect of the phosphoryl groups of grafted ester molecules that interact with the acid sites on the oxide surface, thus efficiently making the surface less accessible to the adsorbate.

The density of grafting of diethyl phosphonates on γ-Al_2O_3 surface was studied in relation to the grafting conditions.[9] The highest grafting density (4.5 – 5.0 nm^{-2}) was achieved upon heating of an alumina – ester slurry at 120 °C for 20 h. It should be noted that, despite all advantages, the procedure requires a consumption of large amount of the modifier. Similar grafting density values were also achieved using a method involving the coating of oxide surface with small amounts (sufficient for the formation of 2 – 3 monolayers) of modifier in a volatile solvent followed by evaporation of the solvent and heating of the support at 120 °C for 20 h. Changes in the pore volume in the support upon modification of Al_2O_3 with phosphonic acid esters were estimated.[9] It was shown that this parameter decreases only slightly (by a few per cent) in the course of modification, which is comparable with the accuracy of its determination.

A number of studies are devoted to adsorption of esters of various phosphorus-containing acids (in particular, dimethyl

§ Diphosphonic acid monolayers themselves almost do not inhibit metal corrosion by 5% hydrochloric acid.

¶ Seemingly, in this case is it possible to avoid destruction of the support, which is observed in the modification of Al_2O_3 with free phosphonic acids or their bis(trimethylsilyl) esters.

methyl phosphate) from the vapour phase on the surfaces of various oxides including Al_2O_3. These studies are of considerable interest because the authors reported a comprehensive study of the interaction between these compounds and the oxide surface.

In particular, chemisorption of phosphoric acid, trimethyl phosphate, methyl and dimethyl methylphosphonates on bare and oxidised (111) faces of alumina was studied.[46] Preliminary chemisorption studies of dimethyl methylphosphonate on the (111) face of platinum,[47] (100) face of rhodium [48] and on alumina surface [49] showed that the process begins with the donor–acceptor interaction of the phosphoryl oxygen atom with the surface. The energy of the donor–acceptor bond formed can be rather high ($\sim$58 kJ mol^{-1} according to Ref. 48). Desorption of such samples occurs only upon heating to high temperatures. Noteworthy is that not dimethyl methylphosphonate but products of its decomposition (H_2, H_2O, CO, CO_2, CH_4 and MeOH) are desorbed. Decomposition of ester molecule begins with cleavage of the P–O(C) bonds followed by cleavage of the P–C bonds at higher temperatures. Taking sorption of trimethyl ester of phosphorous acid on the (110) face of iron as an example, it was shown [50] that sorption is accompanied by the formation of grafted methoxyl groups, which decompose to carbon monoxide and hydrogen at high temperatures.

Adsorption of dimethyl methylphosphonate on the (111) face of aluminium cleaned from the oxide film is accompanied by essential degradation of the ester molecule, as indicated by desorption of alkanes and alkenes from the surface and by the formation of a graphite-containing surface phase. A dimethyl methylphosphonate layer formed on the surface of oxidised aluminium is much more stable. According to X-ray photoelectron spectroscopy data, the ester bonds P–O–C are rapidly cleaved to form Al–O–P bonds while the P–C bond remains stable up to 550 K. [It should be noted that exposures of the gaseous ester to the surface were rather low, namely, from 0.5×10^{-4} to 1.0×10^{-4} Torr s (see Ref. 49).]

Sorption of dimethyl (diisopropyl, diphenyl) methylphosphonates on Al_2O_3 surface was studied by tunnelling electron microscopy.[51] The surface of Al_2O_3 was formed by plasma oxidation of Al films. Experiments were carried out in the temperature interval from 200 to 673 K; the diisopropyl and dimethyl esters were deposited from the gas phase (exposure of 1 Torr s) and the diphenyl ester was applied from 0.025 M solution in hexane.

At sorption temperatures below 295 K, adsorption of the esters on the surface involves formation of donor–acceptor bonds between the phosphoryl oxygen atoms and surface Al atoms. Above 295 K, decomposition of the dimethyl and diphenyl esters begins with cleavage of one ester bond P–O–C and formation of one Al–O–P bond. In other words, layers of grafted methyl methylphosphonate and phenyl methylphosphonate groups are formed on the surface. In the case of diisopropyl ester the process begins only at temperatures above 373 K, which seems to be due to considerable steric hindrance produced by the isopropyl groups. At temperatures above 473 K, the second methoxyl group of the grafted methyl methylphosphonate decomposes and a layer of methylphosphonate groups is formed on the surface (methylphosphonate groups are stable in inert atmosphere up to 750 K). Elimination of the second phenoxyl group from the grafted phenyl methylphosphonate occurs only at 673 K. The mechanism of the interaction of these three esters with Al_2O_3 surface was documented.[51]

A similar study [49] of adsorption of gaseous dimethyl methylphosphonate on the surface of Al_2O_3 film was carried out in the temperature range from 200 to 673 K at exposures from 3×10^{-4} to 10 Torr s. The results obtained were in excellent agreement with the published data [46] on sorption of dimethyl methylphosphonate. It was also pointed that sorption of methyl methylphosphonate proceeds by the same mechanism as sorption of carboxylic acids. In both cases, interaction of the surface hydroxyl group with the proton of carboxylic acid (or methyl methylphosphonate) and interaction of the carbonyl (or phosphoryl) oxygen atom with the surface Lewis acid site is accompanied by the formation of a water molecule and a modifier molecule attached to the surface in bidentate fashion.

Sorption of dimethyl methylphosphonate without dissociation can proceed by two mechanisms.[49] One of them involves formation of hydrogen bonds between the phosphoryl oxygen atoms and surface hydroxyl groups while the other involves formation of a donor–acceptor bond of the same oxygen atom with a surface Lewis acid site. In the latter case the energy of the bond between the ester molecule and alumina surface ($\sim$100–120 kJ mol^{-1}) is about four times higher than in the former. A product of sorption proceeding by the first mechanism can be detected based on the shift of the IR absorption band of the surface hydroxyl groups from 430 to 415 cm^{-1}. Actually, such a product was detected in a study of low-temperature (200 K) sorption of dimethyl methylphosphonate. However, IR spectroscopy data showed that the surface of the starting oxide rapidly takes its initial appearance, from which it follows that almost all amount of ester is desorbed from the surface at this temperature.

One can assume that the preferred mechanism of molecular sorption involves formation of hydrogen bonds. This is in agreement with the fact that at 295 K some amount of chemisorbed ester (product of either donor–acceptor interaction or dissociative sorption) is present on the surface of non-dehydroxylated Al_2O_3 in addition to a rather low concentration of surface Lewis acid sites.

The IR spectra support the dissociative mechanism of sorption. In particular, this is confirmed by the detection of methanol formation. However, it is still unclear whether or not does dissociative sorption follow the donor–acceptor interaction. In order to answer this question, adsorption of trimethylphosphine oxide on the surface of Al_2O_3 was studied.[49] The Lewis basicity of this compound is similar to that of dimethyl methylphosphonate, however trimethylphosphine oxide cannot be dissociatively sorbed under these conditions. It was shown that trimethylphosphine oxide is bound to the surface to a temperature of 473 K, which indicates a strong interaction between the molecule and the surface. At the same time phosphonic acid esters are known to possess relatively low reactivities, so the interaction of inactivated ester molecule with such nucleophiles as the hydroxyl groups of Al_2O_3 surface is unlikely. From this it follows that dissociative adsorption is preceded by the formation of donor–acceptor bonds between the phosphoryl oxygen atom and surface Lewis acid site. Probably, in this case the ester groups displace the water molecules and hydroxyl groups bound to the Lewis acid sites. It was also shown that hydroxylation of the surface has little effect on the results of grafting, thus substantiating the last-mentioned assumption.

Dissociation of the second methoxyl group in methyl methylphosphonate grafted on the surface is difficult to proceed. Even at 673 K, only 60% of methoxyl groups are eliminated from methyl methylphosphonate attached to the surface.

3. Other phosphonic acid derivatives

Chemisorption of isopropyl methylphosphonofluoridate on Al_2O_3 was studied.[52] It was shown that at room temperature the grafting of ester molecules on the surface is accompanied by selective elimination of HF. The grafted molecules gradually decompose, which results in liberation of propene and formation of a monolayer of methylphosphonate molecules on Al_2O_3 surface. At 295 K, the process is rather slow (only $\sim$2% of grafted monoester groups are decomposed) but accelerates on heating.

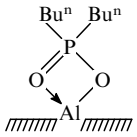
Modification of γ-Al_2O_3 surface with phosphonodichloridates was reported.[9] The dichloridates interact with the surface rapidly under mild conditions. It was found that this type of modification radically changes the granulometric composition of γ-Al_2O_3 particles. Namely, relatively large particles (100–200 μm in diameter) are transformed to fine dust (particles at most 2 μm in diameter). The pore volume in the support abruptly (by an order of magnitude) and uncontrollably (it can either increase or

decrease) changes in the course of modification. These data and an abnormally high grafting density of the phosphonodichloridate molecules (~ 6 nm^{-2}) indicate that the interaction is accompanied by degradation of the particulate surface layer and formation of aluminium phosphonate and, probably, aluminium chloride phases.

The interaction of γ-Al_2O_3 particles with 0.1 M aqueous potassium *n*-octylphosphonate n-$C_8H_{17}P(O)(OK)_2$ was investigated in the same study. It was shown that the salt slowly reacts with γ-Al_2O_3 surface (the grafting density of phosphonate groups is only 1.2 nm^{-2} after 100 h of modification). The modification is accompanied by dispersion of the oxide particles, which indicates degradation of the surface layer.

4. Phosphinic acids

Di-n-butylphosphinic acid interacts with γ-Al_2O_3 to give an aluminium dibutylphosphinate surface layer.[9] The grafting density is very high (4.8 nm^{-2}). The interaction is accompanied by dispersion of the support, being indicative of degradation of the surface oxide layer.



The hydrolytic stability of the coating obtained is relatively high (phosphoryl oxygen atom forms a rather strong donor–acceptor bond with the Lewis acid site), namely, the grafting density remains almost unchanged after two days of treatment with aqueous dioxane in the range of pH values from 2 to 7. However, the grafting density appreciably decreases beyond the limits of this interval of pH values.

IV. Modification of titania surface

Interest of researchers in the chemical modification of titania surface is due to the wide use of metallic titanium owing to unique properties of the material (high strength, corrosion resistance, relatively low density). A significant advantage of titanium consists in its good biocompatibility, which makes it possible to use this material for fabrication of bone prostheses. Being a wide-band semiconductor, titania has found applications in solar energy converters and in photocatalysis.

Modification of TiO_2 surface (metallic titanium is always covered with a dioxide layer) makes it possible to vary the properties of titanium surface over a wide range. Here, conventional organosilicon modifiers are inappropriate because they do not form dense and stable coatings. At the same time organic phosphorus acids and their derivatives readily react with TiO_2 and form dense ordered layers on its surface. Moreover, as in the case of Al_2O_3, these modifiers significantly improve the uniformity and non-specific character of titania surface, *i.e.*, its inability to be involved in any interactions except for the van der Waals ones.

1. Phosphonic acids

A pioneering study on the modification of TiO_2 surface with phosphonic acids dates back to the early 1980s.[53] In the last decade the emphasis was placed on the investigation of fine details of the grafted layer morphology.

Modification of TiO_2 surface with phenylphosphonic acid under different conditions makes it possible to obtain different coatings.[34] At room temperature, treatment of TiO_2 surface causes coordination of the phosphoryl oxygen atom to acid sites of the oxide surface followed by condensation of P–OH and Ti–OH groups (analogously to the interaction with alumina). Modification of TiO_2 with phenylphosphonic acid under severe conditions (boiling in water or toluene in a tube at 120 °C for 24 h) results in the formation of a bulk phase of titanium phosphonate. This phase can be detected in ^{31}P NMR spectra. The amount of titanium phosphonate formed in water exceeds that formed in toluene. The content of carbon in such samples corresponds to a grafting density of 10 nm^{-2}. Reduction of the surface treatment time to 5 h the causes a decrease in the grafting density, which in this case corresponds to a monolayer coverage.

Modification of TiO_2 surface with bis(trimethylsilyl) phenylphosphonate under severe conditions can also lead to formation of bulk phosphonate phase, however the content of this phase is lower compared to the modification with phenylphosphonic acid.[54] The authors assumed that the formation of this phase involves migration of the trimethylsilyl group from the adsorbed modifier molecule to the oxygen atom of titanoxane fragment followed by cleavage of one Ti–O bond. Diethyl phenylphosphonate forms only a monolayer coating on TiO_2 surface under these conditions.

An IR spectroscopic study[54] of the structure of the grafted layers showed that the IR spectra of the samples modified with phenyl phosphonates exhibit neither P=O, Si–C, nor C–O absorption bands. Based on this fact, it was concluded that the molecules of phosphonic acid esters are mainly attached to the surface of TiO_2 in a tridentate fashion. At the same time the IR spectra of the samples modified with phenylphosphonic acid exhibit a P–OH band, which points to bidentate bonding of a fraction of the modifier molecules to the surface (heating of the modified samples at 120 °C leads to disappearance of P–OH groups).

Photolysis of P–C bonds on the surface of the modified samples under the action of soft UV radiation (350 nm) was also investigated in the study cited.[54] It was found that irradiation of the samples placed in water causes cleavage of the P–C bonds and subsequent formation of a surface layer of titanium phosphate, whereas these bonds are retained upon irradiation of the samples placed in toluene.

Modification of TiO_2 surface with octadecylphosphonic acid[7] does not lead to complete coverage; the surface coverage is $\sim 61\%$ of the monolayer (the use of short-chain alkylphosphonic acids causes the formation of dense monolayers).[55] Most likely, the octadecylphosphonic acid molecules are attached to the surface in a bidentate fashion (grafted layer contains free P–OH groups). According to ^{13}C NMR spectroscopy data, these layers are poorly ordered especially in the region of terminal chain segments.

A structure of monolayers formed by molecules of long-chain phosphonic acids deposited on the surface of nanocrystalline titania using Langmuir–Blodgett techniques was reported.[56] Unfortunately, the authors gave no indications of the character of the bonding between the acid molecules and the surface; because of this, it remains unclear whether or not this process can be considered as chemical modification of the surface.

A study of self-assembly of ordered monolayers of phosphonic acids on hydroxylated native oxide layer of metallic titanium[57] showed that monolayers resulted from surface modification performed at room temperature can be removed with ease by washing the samples with organic solvents, *e.g.*, hot tetrahydrofuran. (In this case low surface coverage was explained by inertness of the oxide film on the surface of metallic titanium to phosphonic acids.[58]) Heating of the modified samples at 120 °C significantly improves the stability of the grafted layers, however attempts to fabricate a dense coating in one step failed because of a high content of physisorbed acid molecules on the surface. By repeating the modification–heating–washing cycle it is possible to attain a higher surface coverage. A monolayer coating is formed only after six treatment cycles. Analysis of AFM micrographs showed that the acid molecules chemisorbed on TiO_2 surface form roundish 'islands'. According to IR spectra, the 'islands' are characterised by ordered molecular arrangement similar to crystalline one.

Grafting of ω-carboxyalkylphosphonic acids † on TiO_2 surface occurs selectively and involves formation of a system of Ti−O−P bonds (carboxyl group remains unattacted to the surface). Here, a high surface coverage is attained after a single modification cycle, which was explained by the interactions between carboxyl groups of the modifier molecules.[57] Monolayers thus formed are rather stable and cannot be removed by washing.

The selectivity of grafting of ω-carboxyalkylphosphonic acids $RP(O)(OH)_2$ with $R = (CH_2)_nCO_2H$ on the surface of titania through the phosphonic group was confirmed in a more recent study.[59] The conformations of $(CH_2)_nCO_2H$ chains in the grafted layer formed depends on the chain length. Ordered quasi-crystalline all-*trans* layers ‡ are formed only at $n \geqslant 16$ (proportion of *gauche*-defects in such chains is low). The acid with $n = 12$ also forms a sufficiently ordered layer with preferred *trans*-conformation of chains, but in this case the proportion of *gauche*-defects is high (at room temperature, alkylphosphonic acids with this chain length do not form ordered layers). Acids with shorter chain length form disordered layers. The possibility of polylayer formation on the surface was also reported; however, polylayers are removed by washing the samples with polar solvents (*e.g.*, acetone).

Ordered layers undergo a thermally induced transition from the quasi-crystalline to a 'liquid-like' state. The conformational mobility of alkyl chains in the layers formed by ω-carboxyalkylphosphonic acids is lower compared to that of the layers formed by alkylphosphonic acids with the same number of carbon atoms. This can be explained by the presence of hydrogen bonds between carboxyl groups (according to IR spectroscopy data, all carboxyl groups of the grafted layer are involved in the formation of hydrogen bonds). The hydrogen bonds are completely disordered, which dramatically differs layers formed by such acid molecules from the layers of ω-mercaptoalkylcarboxylic acids on gold nanoparticles.[60, 61]

Similar results were obtained in a study [62] on the modification of titania surface with carboxyalkylphosphonic acids $HO_2C(CH_2)_nPO(OH)_2$, where $n = 2$, 3, 11 and 15. The authors pointed to bidentate bonding of these compounds to the surface through the phosphonate groups because of a large proportion of surface P−OH groups (analogous results were obtained in another study [54]).

A comparative analysis [63] of stability of the grafted layers formed on TiO_2 (anatase) surface treated with octadecylphosphonic acid and various octadecylsilanes [with SiH_3, $SiCl_3$, $Si(OMe)_3$ and $SiMe_2Cl$ anchoring groups] revealed the formation of highly ordered monolayers with grafting densities of 4.3–4.8 nm^{-2} in all cases except for the modification with dimethyloctadecylchlorosilane. Treatment with the latter compound results in the formation of a disordered layer characterised by a low grafting density (about 1.5 nm^{-2}).

The kinetic curves of sorption are similar for all modifiers and show a fast anchoring of the modifier molecules to the surface followed by a slow increase in the grafting density and gradual ordering (in those cases where ordering does occur). The sorption curves obtained are correctly described by a first-order equation with two rate constants differing by 1–2 orders of magnitude. Based on the rate constant values, the anchoring groups can be ordered as follows with respect to their activities: $SiCl_3 \gg PO(OH)_2 > SiMe_2Cl > Si(OMe)_3 > SiH_3$. Two types of interaction between the modifier molecules and the support surface were proposed based on the analysis of the IR spectra of the samples obtained. The modifiers capable of forming horizontal cross-links (unsubstituted trichloro- and trimethoxysilanes) gave highly ordered layers at low surface coverages (40% – 50% of the limiting coverage). This was interpreted [65] as an indication of the 'island' mechanism of modification. Contrary to this, an ordered layer of octadecylphosphonic acid molecules was formed only at high grafting densities, which indicates a uniform surface coverage similar to the case of dimethyloctadecylchlorosilane that does not form ordered layers under the conditions studied. The thermal stability of the grafted layers is rather high, namely, their degradation begins at ~200 °C in air and at 300 °C in inert atmosphere.

The hydrolytic stabilities of the grafted layers formed on the surface of anatase treated with octadecylphosphonic acid, dimethyloctadecylchlorosilane and octadecylsilane were compared.[64] It was established that the layers formed upon modification of anatase surface with dimethyloctadecylchlorosilane are characterised by low stability, namely, the grafted layer is completely removed from the surface after 24 h of storage in a neutral medium at room temperature. The other two layers show higher hydrolytic stabilities, the phosphonate layer being much more stable. Nevertheless, the grafting density of the phosphonate layer decreased by about 15% after seven days of hydrolysis in a neutral medium at room temperature .

A study [65] on the enthalpies of the reactions of phosphonic acids with TiO_2 surface revealed an increase in the enthalpy with an increase in the length of alkyl group. The enthalpy can even take positive values; in this case, the modification reactions are driven by the entropy factor.

2. Phosphonic acid esters

Diethyl phenylphosphonate and bis(trimethylsilyl) phenylphosphonate are also used for the modification of TiO_2 surface.[34] In all cases the diethyl ester formed only monolayer coatings, whereas the bis(trimethylsilyl) ester under severe conditions (boiling with support in toluene) destroyed the oxide surface with the formation of bulk titanium phosphonate phase.

The possibility of using TiO_2 as photocatalyst gave an impetus to studies on the photodegradation of phosphonic acid esters on the surface of TiO_2. A study [66] on the kinetics of photodegradation of the dimethyl and diethyl methylphosphonates in aqueous solutions showed that only physisorption of these compounds occurs on the TiO_2 surface.

Gas-phase photodegradation of dimethyl methylphosphonate supported on glass coated with a TiO_2 layer (ester concentration in air varied from 1 to 90 ppm^{-1}) results in methylphosphonic acid which interacts with the oxide surface.[67] Activity of the photocatalyst drops owing to progressive poisoning of its surface with degradation products, but can be completely recovered after several cycles of washing with distilled water.

In a study [68] of the interaction of dimethyl methylphosphonate, dimethyl phosphite and trimethyl phosphate with the surface of highly disperse TiO_2 it was established that at low temperatures adsorption of these compounds on the surface is accompanied by the formation of hydrogen bonds with surface hydroxyl groups. At higher temperatures, dissociative adsorption with elimination of methoxyl groups is observed, which ceases at $T > 473$ K. At $T > 573$ K, the P−C bonds are cleaved, which results in the formation of a phosphate phase on the TiO_2 surface.

3. Phosphinic acids and their esters

The interaction of diphenylphosphinic acid and its ethyl and trimethylsilyl esters with TiO_2 surface was studied by IR and NMR spectroscopy.[54] From the spectra of the TiO_2 samples modified with ethyl diphenylphosphinate it follows that this modifier forms a monolayer coating on the surface of TiO_2 under the conditions studied. The spectra of the TiO_2 samples treated with diphenylphosphinic acid or trimethylsilyl diphenylphosphinate exhibit complex patterns and are difficult to interpret. The authors suggested the formation of some amount of titanium diphenylphosphinate on the surface in these cases.

† According to IUPAC nomenclature, these compounds are called ω-phosphonoalkanecarboxylic acids.

‡ Probably, the quasi-crystalline state of the grafted layer is stabilised through the formation of hydrogen bonds between carboxyl groups.

V. Modification of zirconia surface

The surface of ZrO_2 is similar in chemical properties to the surface of TiO_2. At the same time there is a number of significant differences between them. In particular, the concentration of hydroxyl groups on the surface of ZrO_2 is nearly 1.5 times higher than on the surface of TiO_2 and the basicity of zirconia surface is also higher than that of amfoteric titania. These features manifest themselves in the modification of ZrO_2 surface with organic acids of phosphorus and their esters.

The structure of a grafted monolayer formed by octadecylphosphonic acid molecules on the surface of ZrO_2 powder has been a subject of detailed NMR studies (Refs 69, 70). ^{31}P NMR spectra indicate a significantly non-uniform structure of the monolayer formed (the peak is rather broad, which points to different fashion of denticity of the bonding between the phosphonate group and the surface). Phosphonate groups on ZrO_2 surface are not strictly immobilised, because the corresponding reorientation time varies in the range 0.1 – 1 s. This is likely due to high ionicity of the Zr – O bond in the surface monolayer of zirconium phosphonate.

^{13}C NMR spectra provide indications of high ordering of alkyl chains in the grafted layer and of transoid conformation for a vast majority of C – C bonds in these chains. At the same time the proportion of *gauche*-defects in the grafted layer is relatively high even at room temperature and increases on heating.

The structure of layers formed on the surface of non-porous ZrO_2 nanopowder (S_{sp} = 40 $m^2\ g^{-1}$) treated with partially deuterated octadecylphosphonic acid (deuterium atoms were introduced at the carbon atom in α-position with respect to phosphonate group) was studied by ^2H NMR spectroscopy at 200 – 340 K.[71] It was shown that at 340 K the mobility of the anchoring phosphonate group is sufficiently high to be detected by solid state ^2H NMR echo technique. It is believed that so high reorientation rates can be explained, in particular, by bulkiness of the phosphonate group and by monodentate fashion of its bonding to the surface. Simulation of NMR spectra also shows that phosphonate groups can be anchored to the surface of ZrO_2 in different mode.

A ^1H NMR study of phosphonate monolayers on zirconia surface showed the possibility of attainment of all-*trans*-arrangement of alkyl chains.[7] Nevertheless, here we do not deal with crystalline layers because of rather loose chain packing and large vibrational amplitudes.

The effect of the temperature and alkyl chain length on the ordering of the films formed on the zirconia surface treated with alkylphosphonic acids n-$C_nH_{2n+1}P(O)(OH)_2$ (n = 8 – 18) was studied.[72] It was found that the acids with n < 16 do not form ordered layers on the surface of ZrO_2 at room temperature. The acids with n = 16 and 18 form layers with almost all-*trans* alkyl chains at room temperature, but the transition temperature of the hexadecylphosphonic acid layer to the disordered state is only slightly higher than room temperature. The transition temperature of a monolayer formed by octadecylphosphonic acid molecules is about 50 °C; however, in this case the alkyl chains are disordered at lower temperatures compared to crystalline zirconium phosphonates with the closest packing of alkyl chains. Close packing of alkyl chains in the layer is hampered by the phosphonate group whose cross-section is ~0.25 nm^2 (*cf.* 0.18 nm^2 for methylene unit).

In the monolayers studied the tilt angle is 31°.[72] This is somewhat smaller than the equilibrium value for alkylphosphonate bound to the surface in a tridentate fashion; however, this deviation can be compensated by strengthening of the van der Waals interactions between alkyl chains in the case in point.

Structures formed on the surface of ZrO_2 nanopowders (two samples with an average particle size of 5 and 30 nm were used) treated with ω-carboxyalkylphosphonic acids with the spacer length of 2, 3, 11 and 15 methylene units were studied.[59, 60] The results obtained were to a great extent similar to those obtained for TiO_2 (see Section IV), however there is a number of distinctions. First, no P – OH groups were detected within the layer grafted on ZrO_2; this probably indicates a stronger anchoring of phosphonate groups to the ZrO_2 surface. Second, a trend to formation of polylayer coatings on ZrO_2 surface is observed (the second and other layers are bound to the surface and first layer through hydrogen and van der Waals bonds). These layers are stable to multiple washing with acetone, while washing with methanol or aqueous acetone results in removal of the second and subsequent layers.

The selectivity of bonding between the modifier molecules and ZrO_2 surface is also lower than in the case of TiO_2 surface. Namely, the surface of the ZrO_2 powder with a particle diameter of 5 nm contains a small amount of ω-carboxyalkylphosphonic acid molecules bound to the surface through the carboxyl group (this was not observed for the powder with a particle diameter of 30 nm).

The formation of octadecylphosphonic acid monolayers on the surfaces of ZrO_2 and zirconated silica was studied.[7] In both cases ordered monolayers were formed, although the end groups of the grafted chains were disordered. The monolayer on zirconated silica is much more ordered than on ZrO_2. The limiting surface coverage on ZrO_2 was not attained (maximum grafting density was ~73% of the limiting value). The grafting density on zirconated silica is only 26% of the theoretical value; this is probably due to nonuniform coating of the silica surface with the ZrO_2 layer (long-chain phosphonic acids do not interact with silica).

A number of structurally similar types of phosphonate groups were found on the surfaces of the modified ZrO_2 samples. This was associated with the presence of different types of sorption sites on the surface of ZrO_2.[7] The formation of a small amount of zirconium phosphonate on the surface of zirconated silica was detected by ^{13}C NMR spectroscopy.

The surface of ZrO_2 was also modified[73] with regioregular amphiphilic polythiophenes containing phosphonic group in side chains.§ It was found that such polythiophenes form self-assembled monolayers on the surface.

A comparison of the structures and hydrolytic stabilities of monolayers formed on the surface of monoclinic ZrO_2 crystal modified with octadecylphosphonic acid and dimethyloctadecylchlorosilane showed[64] that the acid forms highly ordered surface monolayers with a grafting density of 4 – 5 nm^{-2} while the silane forms disordered layers with a grafting density of at most 2.2 nm^{-2}. Hydrolysis was performed using tetrahydrofuran – water mixtures (tetrahydrofuran was added in order to attain better wettability of the modified support). The hydrolytic stability of the layers formed by the modifier with the dimethylchlorosilyl anchoring group is low. Namely, the grafted layer is completely destroyed after 24 h in neutral medium at room temperature. Layers formed by octadecylphosphonic acid molecules are much stronger bound to the surface. Here, an insignificant mass loss (about 2%) was observed after a week of hydrolysis at pH values from 1 to 10 at room temperature. At 65 °C, the stability of layers somewhat decreases but remains rather high.

The thermal stability[19] and the enthalpy of formation[65] of phosphonate layers on ZrO_2 surface are similar to the corresponding parameters of phosphonate layers supported on TiO_2.

VI. Modification of iron oxide surfaces

Studies on the interaction of organophosphorus acids and their esters with iron oxide surfaces are mainly aimed at fabricating stable and thin anticorrosion coatings supported on iron and iron alloys.

§ Multilayered ordered structures that can be formed by such compounds have been documented.[74, 75]

1. Phosphonic acids

Phosphonic acids are widely used for modification of the surfaces of iron (usually, coated with a native oxide layer) and iron oxides. Most studies on the modification of iron surface with phosphonic acids are carried out to solve certain applied problems; however, attention has also been paid to the problem of the structure of the grafted layer. The structure of the octadecylphosphonic acid layer grafted on amorphous Fe_2O_3 particles synthesised [76] by sonication of a solution of iron carbonyl in decane has been reported.[77] Thermogravimetric analysis of the modified Fe_2O_3 particles 5–10 nm in diameter showed that thermal decomposition of the grafted octadecylphosphonate layer occurs at 340 °C. It was established that the phosphonate group is anchored to the surface in at least bidentate fashion and that thermal desorption involves cracking of hydrocarbon chains of the modifier.

The magnetisation of the iron oxide particles coated with octadecylphosphonic acid is three times lower than that of identical samples modified with sulfonic acids and at least an order of magnitude lower than the magnetisation of the starting iron oxide or iron oxide modified with alkanoic acids.[78,79] This was explained by the action of the phosphonic acid molecules that change the spin state of the near-surface Fe^{3+} ions by promoting their transition from the high-spin to the low-spin state (as a result of formation of donor–acceptor bonds between these ions and the phosphoryl groups of the modifier) and by the fact that unoccupied phosphorus d-AOs enhance the magnetic interaction between neighbouring Fe^{3+} ions.

The assumption that the decrease in magnetisation is due to breakdown of Fe_2O_3 particles under the action of phosphonic acid is apparently incorrect. Indeed, sulfonic acids are much stronger than phosphonic acids and surface modification with the former should result in greater reduction of the magnetisation, which is not observed actually. Additionally, the specific surface area of the Fe_2O_3 particles modified with octadecylphosphonic acid is almost the same as that of the particles modified with carboxylic acids (71.5 and 72 $m^2\ g^{-1}$, respectively). An IR study of the structure of the grafted layer showed that it is highly ordered and that the packing of alkyl groups in this layer is similar to crystal packing.

A dramatic decrease in the magnetisation of the iron oxide particles modified with phosphonic acids was also detected in an EPR study.[80] No broadening of the microwave absorption line of the modified particles was observed on cooling (this behaviour is characteristic of superparamagnetic particles).

An electron microscopic study carried out by the same authors [80] showed that the modified particles do not dissolve in phosphonic acids. These results as well as EPR spectroscopy data suggested that the reason for different magnetisation of the starting and modified particles consists in different types of the interaction of surface iron atoms (as was mentioned in Ref. 77). Most probably, antiferromagnetic interactions realise on the surface of the particles modified with phosphonic acids,[81] which eventually leads to superantiferromagnetic particles.[82]

The procedure for self-assembly and derivatisation of monolayers of α,ω-alkanediphosphonic acid molecules on the surfaces of soft and stainless steels [41] is similar to that described in Section III.

2. Phosphonic acid esters

Dimethyl methylphosphonate adsorbed on α-Fe_2O_3 surface from the gas phase at 170 K readily interacts with the oxide surface by the dissociative mechanism involving elimination of methoxyl groups.[11] At 250 K, both methoxyl groups dissociate and a methylphosphonate layer is formed on the surface. Further heating leads to decomposition of the ester with evolution of volatile products (carbon oxides, water, methanol, hydrogen, formic acid) and formation of iron phosphate on the surface. Dissociative chemisorption with elimination of two MeO groups at temperatures above 250 K was also observed in the modification of the (110) face of iron crystal with trimethyl phosphate.[50]

Modification of iron powder with diethyl esters of octyl- and tetradecylphosphonic acids is highly efficient.[20] The coatings obtained exhibited good corrosion resistance (no corrosion was observed even after a few weeks of storage in aerated 0.1 M NaCl solution). The conductivities of the modified powders remained rather high, being almost equal to the conductivity of untreated iron powder freshly cleaned from native oxide film. This indicates that the monolayer coating thus formed presents no difficulties to electron transport (electron tunnelling effect manifests itself at distances of the order of the thickness of monolayer coating). This differs the phosphonate coatings from the triethoxysilane-based ones. The latter also efficiently protect iron from corrosion, but reduce the conductivity by three to six orders of magnitude (probably, due to formation of a thick insulating polymer layer on the surface). The phosphonate coatings also have a high thermal stability, namely, they protect iron from oxidation in air up to 350–400 °C.

VII. Other oxides and metals

The action of diethyl methylphosphonate vapours on tin dioxide at 300 °C causes dissociative sorption of the ester with elimination of ethylene (from one EtO group) and formation of ethyl methylphosphonate layer grafted on SnO_2 surface.[83] Raising the temperature leads to elimination of the second EtO group. Diethyl methylphosphonate is used as a model compound in detecting organophosphorus compounds (in particular, warfare agents) using semiconductor (SnO_2) sensors.[83]

A study [56] of monolayer films formed by eicosylphosphonic acid molecules deposited on SnO_2 surface using Langmuir–Blodgett technique showed that at a surface area per acid molecule of 0.23 nm^2 the tilt angle is 17°; reduction of the surface area to 0.2 nm^2 causes the tilt angle to decrease to 16°. Unfortunately, the nature of bonding between the acid molecules and the SnO_2 surface was not studied; therefore, it is unknown whether the chemical grafting of the acid molecules on the surface or physisorption occurs.

The formation of eicosylphosphonic acid layers on silver and gold supports was also investigated in the study cited,[56] and again the nature of sorption was not studied. However, one can assume that no chemical grafting occurs, because bare gold surfaces do not adsorb phosphonic acids [84] while a layer of phosphonic acid molecules physisorbed on a gold substrate can be removed with ease by washing with organic solvents (even isooctane). Taking into account the fact that monolayer films formed by alkanethiol molecules that readily interact with the surface of gold substrates exhibit not too high oxidation stability (oxidation causes desorption and degradation of the grafted layer), elaboration of methods for modification of gold surfaces remains topical.

A procedure involving deposition of submonolayers formed by copper atoms on the surface of gold supports followed by modification of the surface with phosphonic acids was proposed.[84] A grafted layer thus obtained is stable and cannot be removed from the surface using such solvents as isooctane, ethanol and water. Octadecylphosphonic acid monolayers on copper-plated gold surface show the water and hexadecane contact angles of 111° and 28°, respectively, which indicates a high density and ordering of the layers. This was also substantiated by IR spectroscopy data.

At the same time IR spectroscopy data revealed a larger tilt angle of alkyl groups of octadecylphosphonic acid molecules compared to alkanethiol molecules grafted on gold surface. This is likely due to the fact that the amount of copper on the gold surface is less than that required to provide a monolayer coating. Accordng to X-ray photoelectron spectroscopy data, the copper : oxygen : phosphorus ratio at the surface is 2 : 3 : 1, *i.e.*, there is one phosphonate group per two copper atoms.

The layer formed by octylphosphonic acid molecules on copper-plated gold surface is disordered and has a liquid-like structure.[84] The octadecyl- and octylphosphonic layers are 2 and

0.8 nm thick, respectively (ellipsometry data). Electroactive 11-ferrocenylundecylphosphonic acid can also be grafted on copper-plated gold surface. However it does not form ordered monolayers (probably, due to the bulkiness of the ferrocenyl group, which precludes the close packing of alkyl groups). The density of grafting of ferrocenylundecylphosphonic acid molecules on the surface is 4 μmol m^{-2} (see Ref. 84), which is somewhat lower than the value obtained for thiols (4.3 – 5.6 μmol m^{-2}).[85–88]

The formation of monolayers of α,ω-alkyldiphosphonic acid molecules on the surface of copper, brass, tantalum and chromium was reported.[41] The properties of these monolayers are generally similar to those of corresponding monolayers formed on aluminium and titanium (see Section III). Monolayer films of ω-carboxyalkylphosphonic acids formed on tantalum surface[89] are similar to the layers prepared on aluminium surface (see Section III). Self-assembled monolayers formed by octadecylphosphonic acid molecules on tantalum surface was also studied.[90] A rather high degree of ordering of alkyl groups in these layers is similar to that observed for alkylthiol layers formed on gold surface.

Monolayer films formed by n-amyl- and n-tetradecylphosphonic acid molecules on zinc surface were prepared[91] by treating a polished zinc plate with solutions of corresponding acids in ethanol or aqueous ethanol. Both acids form dense layers, rather highly ordered for C_{14} and much lower ordered (almost disordered) for C_5. The water and hexadecane contact angles for the tetradecylphosphonic acid layer almost coincide with the values characteristic of fully methylated surface, thus confirming high density and ordering character of the layer. Nevertheless, such layers do not protect zinc from electrochemical corrosion.

Dimethyl methylphosphonate vapours interact with tungsten trioxide surface[68] similarly to the case for titania (see Section IV). The only significant difference between sorption of ester on these two substrates is the formation of much stronger hydrogen bonds between the ester phosphoryl group and the surface hydroxyl groups on WO_3. This was attributed to a much higher Brønsted acidity of WO_3 surface compared to TiO_2 surface.

Information on the interaction of phosphonic acids with hafnia-coated silica surface is also available.[92,93]

VIII. Applications of materials with surfaces modified with organophosphorus compounds

1. Separation membranes

One of the key avenues of practical use of phosphonic acids as modifiers of Al_2O_3 and TiO_2 surfaces is fabrication of organoceramic membranes. Such membranes were prepared[94] by chemical grafting of n-butylphosphonic acid on the surface of an alumina membrane. The modification was carried out in order to change the gas transport properties of the membrane, because efficient separation of gases with similar molecular masses using the initial mesoporous membrane with a pore diameter of 5 nm was impossible. Changes in the surface properties of the modified membrane provided a way to controllable variation of the contributions of different transport mechanisms and to improvement of the membrane's permeability and selectivity. n-Butylphosphonic acid modified membranes were used for separation of CH_4, C_2H_6, C_3H_8, N_2, H_2 and CO_2 at room temperature. The best results (high permeability and high selectivity coefficient) were obtained for the separation of a propane – nitrogen mixture. The authors pointed that the n-butylphosphonate layer can be removed from the surface by washing with alkali (in this case the properties of the initial membrane are recovered; if necessary, the membrane can be re-modified).

Membranes for separation of bovine serum albumin from native bovine serum by ultrafiltration were synthesised.[55] When using TiO_2 membranes, albumin is adsorbed irreversibly and cannot be removed from the membrane surface until complete denaturation. However, sorption of albumin becomes reversible upon treatment of the membrane with n-butylphosphonic acid, which forms a monolayer with a grafting density of about 5 μmol m^{-2} on TiO_2 surface (this corresponds to a cross-section area of ~0.3 nm^2). The acid modified membrane is highly hydrophobic, which precludes water transport across the membrane under the experimental conditions. Wetting the membrane with ethanol – water mixture makes the surface hydrophilic and transport of water or aqueous solutions across the membrane becomes possible. This is not accompanied by desorption of butylphosphonate groups from the surface. Albumin is not adsorbed on this membrane, being filtered with a nearly 100% efficiency.

Membranes made of alumina or silica cannot be used because of breakdown of the former and instability of grafted layers on the latter material.[55]

The IR spectra of modified TiO_2 exhibit no P=O and P–OH absorption bands. This was interpreted as an indication of tridentate grafting of butylphosphonic acid molecules. The grafted layer can be removed from the surface by washing with a NaOH solution following a known procedure;[95] this is followed by recovery of the initial properties of the membrane.

Similar results were obtained for a ZrO_2-based membrane.[55]

2. Heterogeneous metal complex catalysts

Phosphonate anchoring groups are used for immobilisation of metal complex catalysts on solid supports. The activity of metal porphyrinate complexes immobilised on TiO_2 surface in the alkene oxidation reactions was studied.[96] Catalysts were prepared by grafting metal porphyrinates with phosphonate groups on TiO_2 surface. The authors also reported the possibility of grafting such complexes on the surface of TiO_2 electrodes, which can be used in electrochemical catalysis and in fabrication of electrochemical sensors.

The synthesis of heterogeneous metal complex catalysts based on bipyridyl complexes of rhodium and iridium grafted on TiO_2 surface was reported.[97] The complexes were grafted through phosphonate groups in the ligand side chains. These compounds exhibit a rather high catalytic activity similar to that of homogeneous analogues. The highest activity was obtained for the complexes immobilised on freshly prepared (by hydrolysis of tetraisopropoxytitanium) titania, whereas grafting on a commercially available oxide (specific surface area of 429 m^2 g^{-1}) gave somewhat less reactive samples.

Phenylphosphine ligands are very often used for the synthesis of catalytically active metal complexes. The possibility of immobilisation of phosphines $Ph_2P(CH_2)_3Si(OEt)_3$ on the surfaces of various inorganic oxides (MgO, TiO_2, Al_2O_3 and SiO_2) was studied.[98] It was found that these phosphines can be easily grafted on the surfaces of Al_2O_3 and SiO_2, but cannot be grafted on the surfaces of TiO_2 or MgO.[98] At the same time similar ligands with phosphonate anchoring groups[99] can be grafted on the surfaces of the last-mentioned two oxides.

The catalyst performance was studied[97] in relation to the pH of the medium. The highest performance was achieved at pH 5.6 and remained unchanged up to pH 12.5 for two days (the authors reported a slight increase in performance), thus indicating stability of the grafted layer at $5.6 \leqslant pH < 12.5$. However, at pH 12.9 the catalyst performance dramatically decreases with time due to degradation of the grafted layer.

3. Modified electrodes

Phosphonic acids are often used for modification of oxide electrode surfaces. In particular, the surface of TiO_2 (anatase) nanocrystals supported on conducting glass was modified with viologen (1,1′-dieicosyl-4,4′-bipyridinium dichloride) and eicosylphosphonic acid.[100] A mixture of eicosylphosphonic acid and viologen was deposited using Langmuir – Blodgett technique. At high dilution of viologen with the acid, only one viologen molecule with known orientation is adsorbed on each TiO_2 nanocrystal and no electron transfer between viologen molecules adsorbed on different nanocrystals occurs. This system can be used as photo-

sensitive electrode for a photoelectrochemical cell (such a cell is highly sensitive in the visible spectral region).

A rather large number of studies are devoted to modification of electrodes fabricated from indium–tin oxide (ITO) ceramics (91% In_2O_3, 9% SnO_2). In particular, ITO electrodes can be modified with phosphonic acids to form a salt monolayer on the surface.[101]

The electrochemical properties of an ITO electrode modified with 2,5-bis(phosphonomethyl)hydroquinone and a ZrO_2-coated ITO electrode were studied [102] by cyclic voltammetry.¶

The molecules of 2,5-bis(phosphonomethyl)hydroquinone spontaneously and irreversibly react with the surface of the ITO electrode irrespective of the presence of a zirconium layer. The grafting density is $\sim$2.6 μmol m^{-2} (about 40% of theoretically possible value). The modified electrodes showed good characteristics in electrochemical molecular recognition of alkali metal and ammonium cations. Namely, they permitted the observation of unique redox peak potential shifts depending on the molar concentration of each type of cations in the range 0.01–1.0 mol $litre^{-1}$. The electrodes are selective to potassium cation in the presence of sodium cations. Initially, the electrochemical characteristics of the non-zirconated modified electrode almost coincides with those of the zirconated electrode, but gradually changes with time (probably, due to a lower hydrolytic stability of the grafted layer on the non-zirconated electrode). The grafted layer on the zirconated electrode was stable at $0 \leqslant pH < 12$.

The interaction of 6-(ferrocenyl)hexylphosphonic acid with the surface of an ITO electrode was studied.[103] This acid can be grafted on the electrode surface (the grafting density is 3.1 μmol m^{-2} or about 70% of the limiting value [104]). The grafted layer is characterised by strong intermolecular interactions between ferrocenyl fragments. Monolayers thus obtained are stable in acetonitrile in both (ferrocene and ferricinium) forms, however protic solvents gradually destroy the grafted layer. As a result, the grafted molecules are desorbed from the surface (the process in ethanol at room temperature is slow while proceeds faster in water). Boiling of the modified samples in water leads to complete desorption of the grafted molecules from the surface.

Owing to strong intermolecular interactions between ferrocenyl fragments the modifier molecules are grafted on the support surface in 'island' fashion even at low surface concentrations. Attempts to obtain a more uniform grafting by 'diluting' 6-(ferrocenyl)hexylphosphonic acid with short-chain phosphonic acids failed. Apparently, ferrocenyl fragments interact with one another much stronger than with short alkyl chains. When dodecylphosphonic acid was used as diluent, a 'dilution' effect was observed, but attempts to efficiently isolate ferrocenyl fragments also failed. Apparently, acids with longer chains should be used in this case.

ITO electrodes are most often used as anodes in organic bilayer based electroluminescent devices, because ITO glass is transparent (optical transmission of 90%) and possesses good conducting properties; various metals can serve as cathodes. Unfortunately, the metals characterised by low work function of electron are highly reactive and readily oxidisable (*e.g.*, calcium or a magnesium/silver alloy), which limits the lifetime of the devices.

Phosphonic acids are known to form self-assembled monolayers on the surface of ITO glass.[105] Using an ITO electrode coated with electron-acceptor 2-chloroethylphosphonic acid and an aluminium cathode, the threshold voltage was considerably reduced [106] to a value characteristic of a much less stable magnesium–silver electrode. The use of the modified ITO electrode eliminates the need of electrodes made of highly reactive metals and makes it possible to exclude a factor that limits the operational life of electroluminescent devices (because the grafted layer of such devices is stable under the operation conditions).

Modification of the ITO electrode with 2-chloroethylphosphonic acid led [107] to considerable improvement of the stability of a light-emitting diode based on poly(5-methoxy-2-octyloxy-1,4-phenylenevinylene) owing to reduction of the onset voltage. Electronic effects at the polymer/ITO electrode interface in the electroluminescent devices based on an ITO electrode modified with 2-chloroethylphosphonic acid were also considered.[108]

4. Biosorbents

Porous beads made of ZrO_2 modified with ethylenediamino-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic) acid were used as pseudoaffinity sorbents for chromatographic separaion of human immunoglobulin G from untreated blood serum.[109] The particle diameter varied from 25 to 38 μm. The effects of the temperature, of sodium chloride content in eluent and of the eluent pH on the maximum binding capacity of the protein and the equilibrium binding constant were studied. Measurements were carried out in the temperature range from 4 to 35 °C at sodium chloride concentrations in the eluent of 0.05, 0.1 and 0.2 mol $litre^{-1}$ and at pH values of 5.5, 6.0, 6.5, 7.0 and 8.0. Temperature changes in the range given above had almost no effect on the binding constant, whereas an increase in the salt concentration or in pH value led to a marked decrease in the maximum binding capacity and to an increase in the binding constant. The maximum binding capacity of immunoglobulin G at the lowest pH value (5.5) is 55 mg ml^{-1} (see †). The sorbent obtained allows immunoglobulins A, G and M in untreated serum to be separated. At a linear elution velocity of 4.32 cm min^{-1}, the yields of these immunoglobulins were reapectively 29.5 ± 6.3, 3.22 ± 0.70 and 6.84 ± 0.70%, respectively. The purity of the immunoglobulins obtained from a single chromatographic run was 89.0 ± 2.6%.

The decrease in the maximum binding capacity with the increase in the electrolyte (sodium chloride) concentration suggests that the binding of immunoglobulin to the sorbent the most important role is played by electrostatic interactions and, probably, hydrogen bonds. The mechanism of the interaction between immunoglobulin and the sorbent is still to be clarified.

At all temperatures studied, the shape of adsorption curves is correctly described by the Langmuir equation. The values of the binding constant indicate a moderate degree of affinity of the sorbent, which is characteristic of pseudoaffinity ligands.[110, 111]

A more recent study on optimisation and modelling of chromatography on this sorbent was reported.[112] The maximum static binding of human immunoglobulin G on this sorbent was 55–65 mg ml^{-1} and the maximum dynamic binding was 12–20 mg ml^{-1}. It was emphasised [112] that ZrO_2 offers significant advantages over conventional silicas and polymeric supports, namely, high strength and excellent thermal and chemical stabilities, which also allows this material to be used as support.[110, 113–115]

The phosphonic acid used for modification is [112] a highly efficient blocker of Lewis acid sites present on the surface of unmodified zirconia in a concentration of 4–5 mmol m^{-2} (see Ref. 116). The sorbent studied also possesses a high hydrolytic stability. Namely, the composition of the grafted layer remained unchanged in the range of pH values from 1 to 10. Possible mechanisms of the pseudoaffinity interaction of the sorbent with immunoglobulin G were also considered.[112]

5. Implants

Titanium is widely used for production of bone implants. One of the key problems concerned with titanium implants is passive integration. No chemical bonds are formed between the growing bone tissue and the implant, which deteriorates the strength of the system at the junction. To increase the adhesive force between the implant and the bone tissue, ethane-1,1,2-triphosphonic and methylenediphosphonic acids were grafted on titanium disks.[117] These disks were used to study proliferation, differentiation and

¶ This electrode was fabricated by pre-soaking of the starting ITO electrode with Zr(IV)-containing solutions.

† Amount of immunoglobulin per ml of sorbent.

protein production for rat osteoblasts (*in vitro* experiments). No statistically significant deviations of proliferation compared to blank run were observed. Thus, the phosphonic acids studied have no cytotoxic effect on osteoblasts. At the same time production of type I collagen on the modified samples increased significantly (up to 16%) compared to non-modified samples, which indicates a stronger binding of the modified implants to the surrounding bone tissue.

Similar results were obtained in a study [118] of the possibility of using modified titanium samples in dental implantology (here, the situation is similar to osteoplastics). Ethane-1,1,2-triphosphonic and propane-1,1,3,3-tetraphosphonic acids were used as modifiers. The results obtained confirmed better biocompatibility of the modified implants, the samples modified with ethane-1,1,2-triphosphonic acid showed a greater sorption of calcium compared to the samples modified with propane-1,1,3,3-tetraphosphonic acid.

6. Magnetic materials for medicine

Magnetite nanoparticles (average diameter 6–8 nm) with grafted biocompatible layers formed by dodecyl- or hexadecylphosphonic acid molecules can find applications in magnetic resonance imaging.[119]

Using IR spectroscopy, it was shown that phosphonic acids form 'islands' with ordered arrangement of alkyl groups and high grafting density on the surface of magnetite nanoparticles. Thermogravimetric analysis (TGA) of the particles fabricated indicates that the phosphonate coatings are more stable than carboxylate ones. From the TGA data it follows that thermal desorption of molecules involves two steps. This was also observed for Fe_2O_3 (Ref. 77) and Ta_2O_5 particles (Ref. 120) and explained by (i) occurrence of two types of the interaction between the modifier molecules and the surface [77, 120] and (ii) formation on the surface of particles of a modifier bilayer similar to the phospholipid layer of biomembranes.[119]

The latter assumption is substantiated by the following facts. First, complete interaction between acids and the surface is difficult to attain; therefore, it is clear that the excess amounts of the acids bound to the surface through weak hydrogen and van der Waals bonds will be desorbed with ease. Second, two-step desorption was observed for not only phosphonic but also carboxylic acids that are attached to the oxide surfaces in a similar fashion.[77] Third, transitions in the differential scanning calorimetry spectra occur at temperatures that correspond to TGA peaks, having a more convex shape in the temperature range corresponding to the second TGA peak. This was interpreted as a substantiation of the formation of a modifier bilayer on the surface of the oxide particles.

7. Anticorrosion coatings

Phosphonic acids are widely used for fabrication of anticorrosion coatings on aluminium, iron and iron alloys. Traditionally, aluminium is protected from corrosion by chromation, which is used in industry on a large scale. However, weak adhesion of chromated aluminium to paintwork materials and toxicity of hexavalent chromium compounds ‡ used for chromation give an impetus to search for and elaboration of alternative methods for protecting aluminium from corrosion. For instance, cellulose derivatives with phosphonate groups were proposed [121] as protective coatings. The surface layers were formed by immersion of metal samples into dilute solutions of phosphorylated cellulose. According to scanning electron mocroscopy data, the surface defects of the starting metal are no longer detected after this treatment. Fourier transform IR data indicate that cellulose units in the surface layers are mainly aligned to the support surface. The properties of the layers formed depend on the concentration of the modifier solution. The thickness of the newly formed layer is $\sim$1 nm in a 0.1% solution and about 6 nm for a concentration of 2%. At concentration of 3% the layer thickness was not determined (according to electron microscopy data, the surface layer has a highly nonuniform structure).

Contact angle measurements showed [121] that after the first immersion the contact angle somewhat decreases, but remains unchanged in the subsequent measurements. The plates modified with the 0.1% solution are characterised by the same contact angle values for the whole surfae area of the sample. Modification with more concentrated solutions results in different contact angle values at different points, thus indicating an inhomogeneous structure of the layers formed using concentrated solutions. These conclusions are also confirmed by corrosion tests. For instance, a thin layer formed from a dilute solution of phosphorylated cellulose is a good protector of aluminium from corrosion, whereas thicker layers prepared from concentrated solutions provide no protection at all (apparently, because of inhomogeneous structure). In spite of positive results obtained [121] it should be noted that chromation of aluminium is a more efficient technique.

It was also proposed to protect aluminium from corrosion using self-assembled layers of organic molecules.[122] Numerous classes of modifiers were studied, namely, aklylphosphates, alkylphosphonic acids, tetraalkylphosphonium salts and alkyliminobis(methylphosphonic) acids, alkyltrimethoxysilanes, alkyldimethylmethoxysilanes, alkanoic acids, aliphatic alcohols, bromides, amines, thiols, sodium alkyl sulfates and sodium alkyl sulfonates. Among them, only monoalkylphosphate, phosphonic acid and trimethoxysilane layers showed good results in studies of their hydrolytic stability at pH values of 7 and 12. Because all other layers possess low hydrolytic stability, only these three types of modifiers were included in further studies.

Contact angle measurements (with water as the process liquid) showed that the silane layers have lower hydrophobicity and corrosion stability than the alkylphosphate and phosphonate layers that are characterised by similar values of the contact angle.

Phosphorus-containing grafted layers thus obtained were studied by IR spectroscopy [122] and it was shown that the anchoring phosphorus-containing group is linked to the alumina surface by three oxygen atoms. For simple alkyl derivatives the degree of ordering of alkyl groups within the grafted layer increases with the treatment time and reaches a limiting value after about 70 h (this is in good agreement with the published data [29]). High grafting density almost equal to the limiting value is reached after a few hours. At the same time bifunctional derivatives containing polar groups in their molecules provide no limiting coverage even after 24 h of modification. The authors failed to estimate the degree of ordering of such layers.

A large number of studies on the modification of metal surfaces with phosphonic acids are devoted to protection of metallic iron from corrosion. In particular, phosphonic acids are used for protection of heat exchangers as both inhibitors of corrosion and heat exchange stabilisers.[123, 124] Due to low toxicity, high chemical stability and ability to inhibit corrosion of iron in neutral media phosphonic acids are widely used as additives to heat-transfer fluid (water).[125, 126] Short-chain phosphonic acids are good inhibitors of corrosion of iron and steels.[124, 127]

The anticorrosion effect of 1-hydroxyethylidenediphosphonic acid (HEDPA) in the presence of calcium cations § on the properties of metallic iron was studied.[128] Treatment of iron with a combination of HEDPA with calcium cations makes it possible to reduce the anodic current and to inhibt the reaction of oxygen reduction at cathode. Using electrochemical methods, X-ray

‡ Special care should be taken when using toxic Cr(VI) derivatives. As time passes, these compounds adsorbed on aluminum diffuse to the environment, thus polluting it.

§ The acid itself is a very poor inhibitor of corrosion of soft steel,[129] while the anticorrosion ability significantly increases in the presence of calcium ions.[130]

photoelectron spectroscopy data and Auger spectroscopy, it was shown that the optimum ratio of the molar concentrations of calcium ions and HEDPA is 1 : 2. As the concentration of calcium cations increases, the corrosion potential is shifted to the cathode.[128]

Synergistic inhibition of corrosion of a soft steel modified with zinc cations and 3-phosphopropionic acid in 0.006% chloride solution was studied[131] by electrochemical and weight change methods. It was found that the grafted layer contains iron phosphonate complexes and zinc hydroxide (it slows the diffusion of iron phosphonate complexes and hydrogen cations through the grafted layer, which in turn inhibits corrosion).

The possibility of protecting iron from corrosion by treatment with phosphonic acids was studied by researchers from another group.[132] The surface of iron was modified at pH 7 with alkylphosphonic and α,ω-alkanediyldiphosphonic acids from aqueous solutions using sodium hydroxide as alkalising agent. It was found that the formation of a surface phosphonate layer changed the polarisation resistance potential and the surface capacitance of the iron sample. The formation of dense grafted layer led to significant inhibition of corrosion (anodic type of protective mechanism).

A study on the kinetics of modification of iron surface with phosphonic acids showed that the process begins with fast adsorption of phosphonic acids and formation of poorly ordered layers. The second stage involves ordering of the grafted layer, as indicated by slow increase in the polarisation resistance. The grafted layer becomes completely ordered after a few days of modification. The major difference between the layers formed by mono- and diphosphonic acids consists in that alkylphosphonic acids form a hydrophobic monolayer coating on the surface, whereas diphosphonic acids can form thin polylayers owing to relatively strong intermolecular interactions.

Piperidin-1-ylmethylphosphonic and piperazin-1,4-diylbis-(methylphosphonic) acids were also used as inhibitors of iron corrosion.[133] The addition of these phosphonic acids causes a shift of the pitting potential in chloride solutions to the region of positive values, which inhibits the pitting attack. The corrosion potential is shifted to the region of negative values and the corrosion current and, hence, the corrosion rate decrease. This was explained by the formation of a dense protective film from phosphonic acid molecules on the electrode surface. It was found that the efficiency of both acids increases as their concentrations in solution increase and reaches a maximum at a concentration of ~ 5 mmol litre^{-1}. Piperazin-1,4-diylbis(methylphosphonic) acid was also shown to be a more efficient inhibitor of corrosion compared to piperidin-1-ylmethylenephosphonic acid.

Inhibition of iron corrosion in hot potassium hydrocarbonate solution (it is often used for absorption of CO_2) was studied.[134] Since HEDPA is also a good inhibitor of soft steel corrosion,[135] it was interesting to consider the inhibiting effect of this acid on stainless steel corrosion. It was found[134] that HEDPA does inhibit corrosion of stainless steel. The addition of small amounts of 2-aminothiophenol to HEDPA significantly enhances the inhibiting effect. Diethanolamine also enhances the protective effect. The best results were obtained with a ternary mixture 2-aminothiophenol/HEDPA/diethanolamine (1 : 10 : 30 000); this mixture is also a good inhibitor of soft steel corrosion.

8. Maintenance of adhesion

In a study[89] on adhesion of organic compounds to metal surfaces it was pointed that ω-functionalised phosphonic acids possess good adhesive properties to aluminium. Phosphorylation provides a good alternative to chromation. In particular, the formation of a phosphonate monolayer on aluminium surface takes only 20 min.[89]

Phosphonic acids can be used as components of base coatings for iron. Such coatings improve the adhesion of varnishes and paints to the metal surface. In a study[136] on novel base coating systems for iron and soft steels the major components were dodecylphosphonic acid and a number of phosphonic acids containing thienyl groups. They form self-assembled monolayers on the passivated iron surface. The samples were coated by immersion into aqueous solutions of modifiers. Prior to modification, iron was treated with 10% HNO_3 solution for pasivation.

The formation of self-assembled monolayers of thienylphosphonic acid molecules on the surface was confirmed by voltammetry and contact angle measurements. Measurements showed an efficient hydrophobisation of iron surface. The water contact angle is $18.5 \pm 4.0^\circ$ for passivated iron, $51.4 \pm 4.0^\circ$ for non-passivated iron and 121.2 ± 2.0 and $148.5 \pm 3.0^\circ$ for iron treated with 6-(3-bithienyl)hexylphosphonic acid and dodecylphosphonic acid, respectively. Large contact angles indicate the formation of dense and ordered layers on the iron surface. Despite the larger contact angle obtained for iron treated with dodecylphosphonic acid compared to iron treated with thienylphosphonic acids, the use of the last-mentioned compounds makes it possible to carry out polymerisation of thienyl groups and thus to improve the stability of the grafted layer.

Adhesion of organic compounds to the surface of titanium can also be improved by phosphorylation.[89]

IX. Conclusion

The published data considered in this review show that phosphonic acids and their esters, as well as phosphinic acids are important and promising modifiers of oxide surfaces. Often, organophosphorus compounds provide the possibility of fabrication of highly ordered surface monolayers with grafting densities approaching the limiting values. By and large, phosphonic acids are more preferable than phosphinic acids because they form more ordered grafted layers and and are more synthetically accessible. Despite the fact that phosphonic acid esters are less reactive than the parent acids, the former are quite often used for modification of oxides (in particular, alumina), because they do not destroy the surface of this support.

It should be noted that organophosphorus compounds are the best modifiers of titania ana zirconia. They form grafted layers of better quality compared to organosilicon compounds. Phosphonic acids are similar to silanes in efficiency of the modification of alumina and iron oxide surfaces. Phosphorus-containing layers grafted on these oxides are more dense, but have a lower hydrolytic stability. If alumina is used under anhydrous conditions, it can be protected with organophosphorus compounds. Silica can be better protected with silanes rather than organophosphorus modifiers because the latter provide a lower grafting density and have a much lower hydrolytic stability, although can form highly ordered layers on the silica surface.

In spite of intensive research in the field in question, many problems are still to be solved, *e.g.*, the mechanisms of the interaction of phosphonic acid esters with the surface of TiO_2. The effects of the crystal structure of Al_2O_3 and TiO_2 on the results of surface modification are also poorly studied. At present, only a narrow range of oxide surfaces can be modified with phosphonic acids and their esters. These are the mineral supports considered in this review.

Organophosphorus modifiers of oxide surfaces are thought to be quite promising for practical use in chemistry, biology and medicine. It is believed that they will be useful for fabrication of selective chemical sensors, in particular, those based on semiconductor SnO_2;[137, 138] efficient titania-based photocatalysts;[139] biocompatible titanium, tantalum and calcium-phosphate implants with grafted phosphonate layers;[140, 141] asymmetric heterogeneous metal complex catalysts;[142, 143] very thin and stable anticorrosion coatings;[144] specific sorbents for separation and concentration of biomolecules;[145] materials for molecular recognition,[146] *etc.*

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