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Theoretical study of organic-inorganic hybrids obtained by grafting reaction of vinyl phosphonic acid on titanium oxide

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The surface modification of an inorganic support with organophosphorus coupling agents is an extremely versatile route to hybrid materials. This route has been applied to a variety of supports, including metal oxides. This paper presents a theoretical study of grafting reaction of the vinyl phosphonic acid on titanium oxide. Formation of three types of hybrids: monodentate, bidentate and tridentate was considered. These hybrids were energy minimized by the semiempirical PM6 method in vacuum. A monodentate hybrid was found as most stable. Lower temperatures favour the hybrid formation. The obtained results gave indications on the complex stability.

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1. Introduction

Organophosphorus compounds (phosphate, phosphonate, or phosphinate compounds) offer a promisssing alternative in the coupling of organic components to metal oxides other than silica [1]. The modification of the surface of TiO_2 particles with phosphonic acids $RPO(OH)_2$ is currently attracting growing interest for numerous applications such as self-assembled monolayers, ceramic membranes, photoelectrochemical cells based on nanocrystalline films of TiO_2, optical write-read-erase devices and enzymatic catalyses.

The anchoring of organophosphorus derivatives on a titania surface is expected to involve both coordination of the phosphoryl oxygen to Lewis acid sites and condensation reactions between the surface hydroxyl groups Ti-OH and the P-OX (X=H, Me_3Si, Et) groups [1, 2]. Accordingly, the possible bonding modes can be mono-, bi-, or tridentate for the phosphonate derivatives and mono- and bidentate for the phosphinate derivatives [1].

$$\text{Ti-OH} + \text{P-O-X} \rightarrow \text{Ti-O-P} + \text{X-OH}$$
$$\text{X} = \text{H, SiMe}_3\text{, Et} \qquad (1)$$

The bonding mode of organophosphorus coupling agent surface species appears to depend strongly on the nature of both organophosphorus coupling agents and the surface, and on the conditions of the surface modification [3]. In the case of phosphonic and phosphinic acids it was shown that, depending on the oxide chemical stability and on the grafting conditions (temperature pH, concentration of organophosphorus coupling agents), a dissolution-precipitation mechanism can be operative, leading to the formation of a metal phosphonate of phosphinate phase, even in case of chemically stable TiO_2. This mechanism implies the cleavage of the Ti-O-Ti bridges by the organophosphorus acid; considering the excellent chemical stability of TiO_2, assistance to the cleavage by coordination of phosphoryl group was proposed.

Regardless of the type of phosphonate coupling molecule used, the main bonding mode to the surface should involve tridentate $PhP(OTi)_3$ units [1, 3]. Covalent anchoring to the surface of phosphonic acids and dimethyl phosphonates on TiO_2 should be taken into account in the reaction pathways [1]. Homocondensation of phosphonate or phosphinate coupling molecules with the formation of P-O-P bridges is unlikely, and such bridges would not be stable in the presence of water. In the case of organophosphorus coupling molecules, reaction with the surface involves not only condensation with surface hydroxyl groups but also coordination of the phosphoryl on Lewis acid sites, and depending on the anchoring conditions, cleavage of the metal-O-metal bonds. One drawback of phosphonic acids is the formation at high temperature and concentration of metal phosphonate bulk phase.

Hydrogen bonds between surface hydroxyl groups and residual P-OH and P=O groups may also be involved [2]. The organic groups are bonded to the inorganic part through metal-O-P bonds only. Thus, the use of organophosphorus coupling molecules in sol-gel processing is very attractive for the preparation of highly homogeneous hybrid materials. Surface modification of inorganic substrates by organophosphorus acids or their salts can be performed in water, contrary to organosilane coupling agents. The formation of multilayers by homocondensation can be discarded, and under mild conditions only monolayers can be formed. However, a dissolution-precipitation process, leading to the formation of metal phosphonate of phosphinate phases, can occur

depending on the chemical stability of the inorganic substrate and the reaction conditions.

This paper presents a study of organic-inorganic hybrids obtained by grafting reaction of vinyl phosphonic acid on titanium oxide by semiempirical quantum-chemical calculations.

2. Methods

2.1 Rutile crystal structure

Titanium oxides have been used extensively in many applications, such as in catalysis, photocatalysis and photoelectrochemical processes [4].

Titanium, the second most abundant transition metal in the earth's crust, is commonly found as the TiO_2 polymorph, rutile [5]. Its oxidation state is usually +4 and its coordination is commonly six-fold, although +3 oxidation and four-fold coordination do occur. Rutile is tetragonal, but the distortion of the coordination polyhedra is fairly small (2 Ti-O distances are of 1.988 Å and 4 are of 1.944 Å).

Knowledge of the structure of oxide surfaces is important for understanding chemical reactions on interfaces [6]. The formal description of surface reactions demands the introduction of a specific chemical component, a so-called ‘‘surface site,’’ which has the ability to react with different ions of the solution. The number of sites on the oxide surface is a very important parameter of surface complexation modelling. In addition, consideration of the surface structure is useful for determining the stoichiometry and mechanism of surface reactions.

In principle, the ideal approach to the simulation of mineral-aqueous interfaces would be to use the detailed surface protonation behaviour, i.e., the actual acid-base reactions and water dissociation processes occurring at the mineral surface [7]. Moreover the chemical interaction of water with the mineral surface involves water dissociation and a variety of acid-base reactions involving successive surface protonation states (proton speciation at the surface).

The nonhydroxylated (110) surface stems from the relaxation of the rutile bulk structure cleaved by the (110) plane [7]. Only rows of bridging oxygens (each bonded to two underlying Ti atoms) protrude out of the layer containing surface titanium and oxygen atoms. In between these rows there are rows of 3-fold coordinated O and 5-fold coordinated terminal TiV atoms in the same surface plane. The length of the bond between bridging oxygen (BO) and Ti atoms was found by *ab initio* calculations to be 1.87 Å.

Brown et al [8] consider that the most important geometric property of any surface is the coordinative unsaturation of its surface atoms and ions. In the bulk rutile structure, all metal cations are in (slightly distorted) octahedral sites, coordinated by six oxygen anions. The thermodynamically most stable rutile face is (110), in which one-half of the surface cations retain their bulk O ion coordination, and the other half are 5-fold coordinated. Less stable is the (100) face, in which all surface cations have 5-fold coordination. The least stable low-index face of rutile is (001), in which all surface cations have only four oxygen ligands. Much of the surface chemistry of oxides is driven by the coordinative unsaturation of surface ions.

Rutile has a simple structure and it is very stable over a broad range of pressure, temperature and pH [9]. Rutile (110) surface has three possible terminating planes theoretically. The first terminating plane has both a surface oxygen bonded to two Ti atoms (BO) and an oxygen singly bonded to the surface (named terminal oxygen or TO) present on the surface. The second terminating plane is ended with only BO atoms present on the surface. The third terminating plane is finished with neither BO or TO, but only a bare Ti-O plane, which was defined as the surface Ti-O plane. Based on the crystal symmetry and the charge balance, the second terminating plane was considered to be favoured in vacuum. A simplified consideration is that when a rutile crystal is cleaved at this position, the stable rutile (110) surface observed in vacuum is obtained, having identical two newly created surfaces and neutral charge. There are two kinds of Ti atom positions on such a surface. One is fully six-coordinated Ti, which is bonded to two BO atoms. The other is five-fold coordinated Ti atom where one longer Ti-O bond is broken.

Many simulations/calculations of water adsorption on rutile (110) surfaces were performed [9]. Contrary to experimental results, most studies indicate that water dissociatively adsorbs even on the defect-free surface. Calculations of multilayer water adsorbed on rutile surface were also reported in a few cases. A layered adsorbed water structure with hydrogen bonding chain structure was proposed.

2.2 Structure of titanium oxide and hybrids obtained by grafting the vinyl phosphonic acid on titanium oxide

The structure of the unit cell of the titanium oxide crystal determined by experimental X-ray crystallography [10] is presented in Fig. 1. Starting from this structure a fragment of hydrated titanium oxide crystal was built by the Hyperchem package [11], taking into account the most stable 110 plane of the unit cell (Fig. 2).

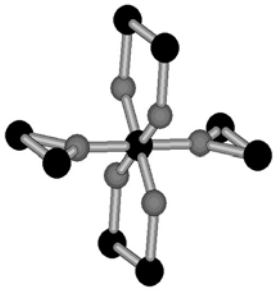


Fig. 1. Structure of the unit cell of the titanium oxide crystal [10].

-oxygen atom; -titanium atom

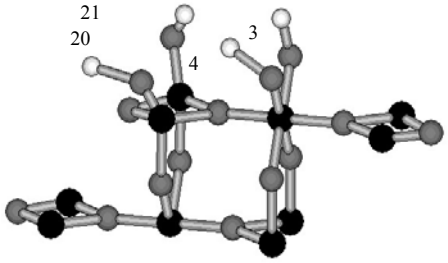
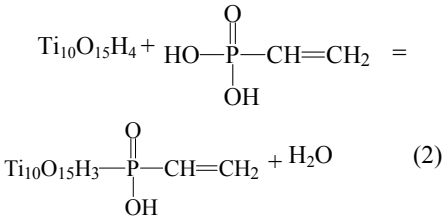


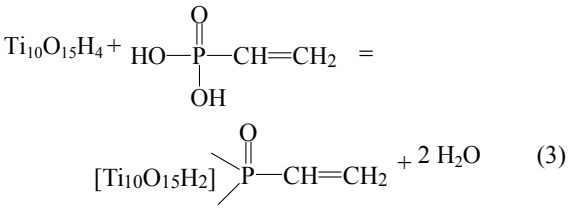
Fig. 2. Structure of the hydrated crystal fragment of titanium oxide built from experimental crystallographic data
-hydrogen atom; - oxygen atom; -titanium atom

Several hybrids of the vinyl phosphonic acid have been built by the Winmostar program [12] taking into account the hydrated crystal fragment of titanium oxide considered above. Following reactions of hybrid formation were considered:



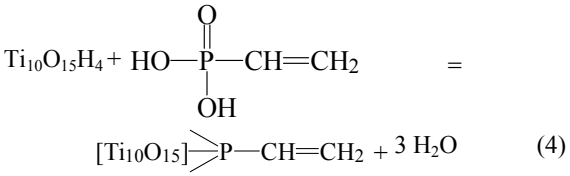
(2)

(M)



(3)

(B)



(4)

(T)

where M represents the monodentate hybrid, B – the bidentate hybrid, T – the tridentate hybrid.

The hybrid structures thus considered were then energy minimized in vacuum by the PM6 semiempirical method included in the MOPAC 2007 program [13]. The keyword PRECISE and a gradient of 10^{-1} were used. From these calculations the enthalpies of formation at 298 K were obtained (see table 1). The vacuum reaction enthalpy of each hybrid at 298 K was then calculated (see table 1). The structures of minimum energy thus obtained were then used for the calculation of thermodynamic parameters by the MOPAC 2007 program [13].

Table 1. Hybrid structures (M = monodentate, B = bidentate, T = tridentate) formed by vinyl phosphonic acid grafting on titanium oxide, enthalpy of formation at 298 K (ΔH_f), hybrid fraction with respect to each type of hybrid (f_1), hybrid fraction with respect to all types of hybrids (f_2).

No.	Hybrid name*	ΔH_f (kcal/mol)	ΔH_r (kcal/mol)	f_1	f_2
1	M_1 (O21)	-1716.86	-82.70	1.32×10^{-81}	1.32×10^{-81}
2	M_2 (O20)	-1827.54	-193.39	1	1
3	M_3 (O3)	-1754.06	-119.90	1.88×10^{-54}	1.88×10^{-54}
4	M_4 (O4)	-1684.82	-50.67	4.54×10^{-105}	4.54×10^{-105}
5	B_1 (O21, O20)	-1594.63	-14.78	2.05×10^{-126}	5.73×10^{-171}
6	B_2 (O3, O4)	-1683.02	-103.18	8.68×10^{-62}	2.43×10^{-106}
7	B_3 (O21, O3)	-1624.99	-45.15	3.28×10^{-104}	9.19×10^{-149}
8	B_4 (O20, O4)	-1611.64	-31.79	5.56×10^{-114}	1.56×10^{-158}
9	B_5 (O20, O3)	-1766.54	-186.69	1	2.79×10^{-45}
10	B_6 (O21, O4)	-1683.62	-103.77	2.37×10^{-61}	6.63×10^{-106}
11	T_1 (O21, O20, O4)	-1609.15	-83.61	2.16×10^{-66}	2.38×10^{-160}
12	T_2 (O21, O3, O4)	-1626.05	-100.50	4.85×10^{-54}	5.34×10^{-148}
13	T_3 (O21, O20, O3)	-1685.25	-159.70	9.32×10^{-11}	1.03×10^{-104}
14	T_4 (O20, O3, O4)	-1698.97	-173.43	1	1.10×10^{-94}

* in parenthesis position of oxygen atoms of hydrated titanium oxide (see Fig. 2) involved in the hybrid construction are given

3. Results and discussion

For a distribution of n low energy hybrids in a given sample, the fraction f_i of a specific hybrid was expressed by the Boltzmann distribution [14, 15], according to the following equation:

$$f_i = \frac{e^{-\frac{E_i}{RT}}}{\sum_{j=1}^{n} e^{-\frac{E_j}{RT}}} \quad (5)$$

where E_i represents the formation enthalpy of the i^{th} hybrid

T – the temperature

R – the universal gas constant

E_j – the total energy (which is proportional to the formation enthalpy) of the j^{th} hybrid

n – number of hybrids

The Boltzmann factor f_i is a weight function related to the percentage contribution of a given conformation to the conformational population of this compound.

From the calculated reaction enthalpies at 298 K of each hybrid (see Table 1) hybrid M_2 had the most negative value of the reaction enthalpy-with respect to the monodentate hybrids, hybrid B_5-with respect to the bidentate hybrids and T_4-with respect to the tridentate hybrids. Taking into account the enthalpy of formation at 298 K with respect to the number of hybrids, the hybrid f_1 fraction was calculated with respect to each type of hybrid (see Table 1). The f_1 values confirmed that the most stable hybrids were the M_2, B_5 and T_4 hybrids, respectively.

The f_2 fraction of each hybrid with respect to the total number of hybrids of all types was calculated, neglecting the difference of one, respectively two hydrogen atoms between the different types of hybrids (see Table 1). The f_2 values indicate as most stable the M_2 monodentate hybrid, in accordance to the biggest negative value of the reaction enthalpy.

Figs. 3-6 present the energy minimized structures of the hydrated titanium oxide, of the M_2 monodentate, B_5 bidentate and T_4 tridentate hybrids obtained by the PM6 hamiltonian.

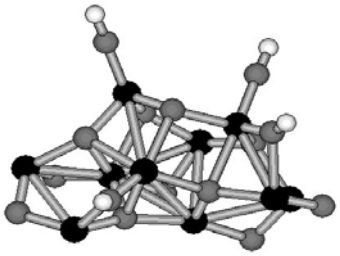


Fig. 3. Energy minimized structure of the hydrated titanium oxide by the PM6 hamiltonian
-hydrogen atom; -phosphorus atom; - oxygen atom; - titanium atom.

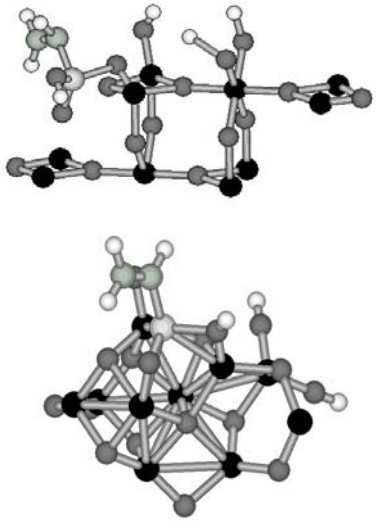


Fig. 4. Energy minimized structure of monodentate hybrid M_2 before (left) and after (right) minimization by the PM6 hamiltonian
-hydrogen atom; -carbon atom; -phosphorus atom; - oxygen atom; -titanium atom

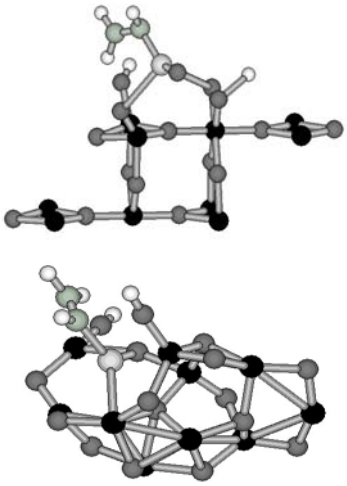


Fig. 5. Energy minimized structure of bidentate hybrid B_5 before (left) and after (right) minimization by the PM6 hamiltonian
- hydrogen atom; -carbon atom; -phosphorus atom; - oxygen atom; -titanium atom

The minimum energy structures thus obtained, of reactants (titanium oxide and vinyl phosphonic acid) and of reaction products (the hybrid and water) were further used for the calculation by the MOPAC 2007 program [13] of some thermodynamic parameters in the range of temperatures from 300 until 400 K, like: formation enthalpy and enthalpy. Table 2 presents the above mentioned thermodynamic parameters calculated for the M_2 hybrid. Low temperatures favour the hybrid formation,

as seen from the dependence of the heat of reaction versus temperature (see Fig. 7).

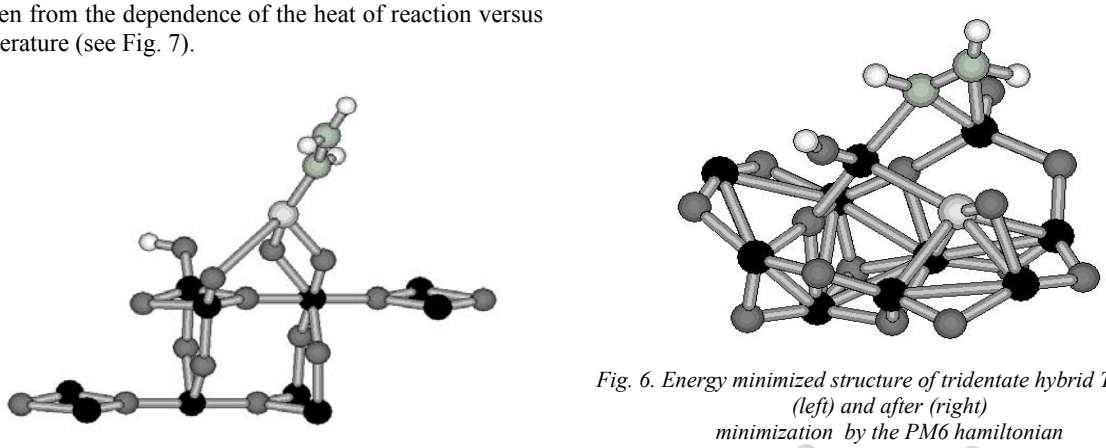


Fig. 6. Energy minimized structure of tridentate hybrid T_4 before (left) and after (right) minimization by the PM6 hamiltonian
- hydrogen atom; -carbon atom; -phosphorus atom; - oxygen atom; -titanium atom

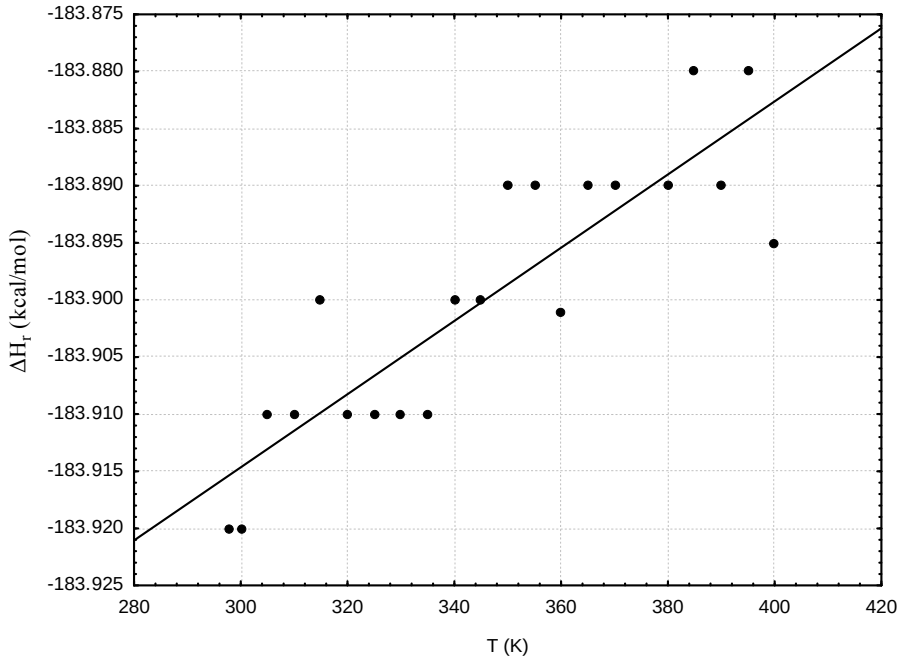


Fig. 7. Dependence of the reaction enthalpy versus temperature for hybrid M_2.

Structural descriptors, like: the solvent accessible surface and volume and the van der Waals surface and volume [16] of energy minimized hybrids have been calculated by the Winmostar program [12]. For the M_2 hybrid following structural parameters were obtained: the van der Waals surface of 422.91 Å^2, the van der Waals volume of 375.28 Å^3, the van der Waals radius of 8.08 Å, the solvent accessible surface of 617.22 Å^2, the solvent accessible volume of 1083.03 Å^3 and the solvent accessible radius of 9.48 Å (the last three ones calculated for water used as solvent, with the water radius of 1.4 Å).

Table 2. Standard formation enthalpy (ΔH_f) of titanium oxide, vinyl phosphonic acid, M_2 minimized hybrid, and water in the of temperature (T) range 300-400 K.

T (K)	ΔH_f (kcal/mol)			
	Titanium oxide	Vinyl phosphonic acid	M_2	H_2O
300	-1502.35	-157.49	-1789.47	-54.29
305	-1501.82	-157.37	-1788.85	-54.25
310	-1501.29	-157.24	-1788.23	-54.21
315	-1500.75	-157.11	-1787.59	-54.17
320	-1500.21	-156.97	-1786.96	-54.13
325	-1499.66	-156.84	-1786.32	-54.09
330	-1499.11	-156.71	-1785.68	-54.05
335	-1498.56	-156.57	-1785.03	-54.01
340	-1498.00	-156.44	-1784.37	-53.97
345	-1497.44	-156.29	-1783.71	-53.92
350	-1496.88	-156.16	-1783.05	-53.88
355	-1496.31	-156.02	-1782.38	-53.84
360	-1495.74	-155.87	-1781.71	-53.801
365	-1495.17	-155.73	-1781.03	-53.76
370	-1494.59	-155.59	-1780.35	-53.72
375	-1494.01	-155.44	-1779.66	-53.38
380	-1493.43	-155.29	-1778.97	-53.64
385	-1492.84	-155.15	-1778.28	-53.59
390	-1492.25	-154.99	-1777.58	-53.55
395	-1491.66	-154.85	-1776.88	-53.51
400	-1491.06	-154.69	-1776.18	-53.47

4. Conclusions

The semiempirical PM6 method was used for modelling the hybrid formation by the vinyl phosphonic acid grafting on titanium oxide. A fragment of titanium oxide structure was built starting from experimental X-ray data. Formation of three types of hybrids: monodentate, bidentate and tridentate was considered. These hybrids were energy minimized by the PM6 hamiltonian in vacuum at the temperature of 298 K. From the formation enthalpies thus obtained reaction enthalpies at this temperature were calculated. These values together with the partition functions calculated for these hybrids indicated the highest probability of monodentate hybrid formation. The energy minimized structures were further used for the calculation of the reaction enthalpy in the temperature range 300-400 and of some thermodynamic parameters for the most stable monodentate hybrid. It was observed that lower temperatures favour the hybrid formation. Structural descriptors, like: the solvent accessible surface and volume and the van der Waals surface and volume of monodentate energy minimized hybrid have been calculated for future structure-property relationships.

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