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Simulation of grafting reaction of benzyl phosphonic acid on titanium oxide by the semiempirical PM6 approach

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Organophosphorus compounds offer a promisssing alternative in the coupling of organic components to metal oxides. It was found that organophosphorus coupling agents can bind strongly to the surface of transition metal oxides. This paper presents a theoretical study of grafting reactions of the benzyl phosphonic acid with titanium oxide. Starting from experimental X-ray data of the rutile crystal, several possible complexes with the benzyl phosphonic acid were built. The semiempirical PM6 quantum chemical approach was used in vacuum in order to find out the way of anchoring. A bidentate hybrid was found as most stable. The results thus obtained gave indications on the stability of the complex formation.

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1. Introduction

Organophosphorus compounds can be considered as an alternative in the coupling of organic components to metal oxides [1]. The surface of TiO_2 particles can be modified by phosphonic acids $RPO(OH)_2$, this modification having several applications, like: self-assembled monolayers, ceramic membranes, photoelectrochemical cells based on nanocrystalline films of TiO_2, optical write-read-erase devices and enzymatic catalyses.

Mutin et al [1, 2] consider that 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. Therefore, the phosphonate derivatives could be bonded as mono-, bi-, or tridentate and as mono- and bidentate for the phosphinate derivatives [1].

The surface modification of an inorganic support with organophosphorus coupling agents (OPCA) is an important way to hybrid materials, as stated by Vioux et al [3]. This route has been applied to a variety of supports, including metal oxides, metals, aluminosilicates, silica, metal hydroxides, and carbonates.

In a previous study [4] the grafting reaction of vinyl phosphonic acid on titanium oxide was modelled by PM6 [5]. The monodentate hybrid was found as most stable of all the studied hybrids.

In this paper we simulate the grafting reaction of the benzyl phosphonic acid with titanium oxide by the semiempirical PM6 method. Several possible hybrids were considered and energy minimized by PM6 in vacuum in the range of temperatures from 298 until 400 K. The reaction enthalpies were calculated from the formation enthalpies thus obtained. The results gave indications on the influence of temperature and on the stability of the complex formation.

2. Methods

2.1 Rutile crystal structure

Titanium oxides have been successfully used in many applications, such as in catalysis, photocatalysis and photoelectrochemical processes [6].

Titanium is commonly found as the TiO_2 polymorph, rutile [7] and 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 [8]. The first hypothesis was that the reaction site of oxide solution interfaces is the surface hydroxide ion formed due to the chemical sorption of a water molecule. The surface structures are obvious for layered minerals but are very questionable for other minerals. In some cases, crystallographic data and common sense allow deduction of the different variants of atomic arrangement on the surface.

The nonhydroxylated (110) surface stems from the relaxation of the rutile bulk structure cleaved by the (110) plane [9]. 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 most important geometric property of any surface is the coordinative unsaturation of its surface atoms and ions [10]. 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; experimentally this face on TiO_2 is found to facet easily into planes containing a higher ligand coordination of the cations.

There are two kinds of Ti atom positions on such a surface [11]. 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.

2.2. Hybrid construction

Structure of hybrids obtained by grafting benzyl phosphonic acid on titanium oxide was built based on experimental data of titanium oxide crystal structure [12]. A hydrated titanium oxide crystal was built by the Hyperchem package [13], taking into account the most stable 110 plane of the unit cell from the unit cell of the titanium oxide crystal [12] (see Fig. 1).

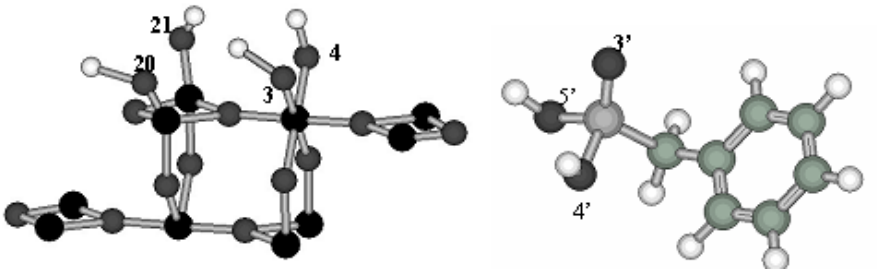
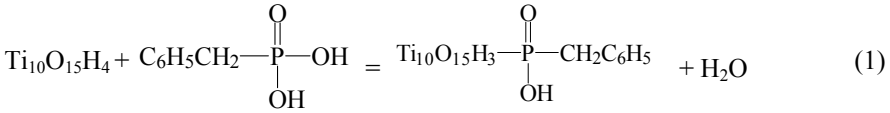


Fig. 1. Structure of the hydrated crystal fragment of titanium oxide built from experimental crystallographic data (left) and of the optimized benzyl phosphonic acid molecule (right).

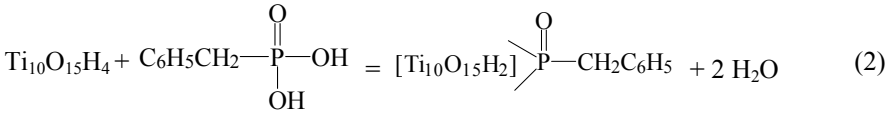
Stewart [5] indicates that the length which involves oxygen forming a dative bond to titanium obtained by PM6 in coordination complexes is typically too long, by 0.1 to 0.3 Å, but the PM6 approach has a better accuracy in predicting heats of formation for compounds of interest in biochemistry in comparison to Hartree Fock or B3LYP DFT methods, using the 6-31G(d) basis set.

Several hybrids of the benzyl phosphonic acid have been constructed by the Winmostar [14] and Vega ZZ v. 2.0.8.60 [15] programs. Following reactions of hybrid formation were considered:



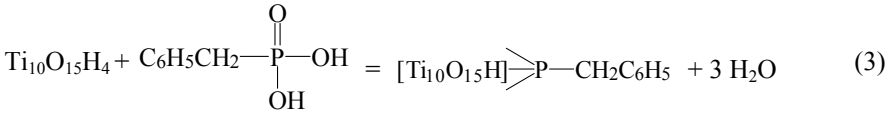
(1)

(M)



(2)

(B)



(3)

(T)

where M represents the monodentate hybrid, B – the bidentate hybrid, T – the tridentate hybrid. In addition, hybrids formed by coordinative bonds between the phosphoryl oxygen atoms and titanium atoms were considered too. Hybrids M_{12}, M_{13} and M_{14} (see table 1) were similar to the hybrids M_9, M_{10} and M_{11}, except the position of the benzyl phosphonic acid, which was rotated to a mirror image position.

The benzyl phosphonic acid was energy minimized in simulated vacuum by the PM6 semiempirical method included in the MOPAC 2007 program [5]. The keyword PRECISE, SCF convergence of 10^{-10} and a gradient of 10^{-2} were used. The minimal energy benzyl phosphonic acid conformation was further used in hybrid construction.

The hybrid structures were energy minimized in vacuum by the PM6 semiempirical method included in the MOPAC 2007 program [5]. 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 further used for the calculation of the reaction heat at different temperatures.

Table 1. Hybrid structures (M = monodentate, B = bidentate, T = tridentate) formed by grafting benzyl phosphonic acid on titanium oxide, enthalpy of formation at 298 k (ΔH_f), reaction enthalpy at 298 k (ΔH_r).

No.	Hybrid name*	ΔH_f (kcal/mol)	ΔH_r (kcal/mol)
1	M_1 (O20*-O4'**)	-1568.64	77.92
2	M_2 (O21*-O4'**)	-1673.58	-27.02
3	M_3 (O4*-O4'**)	-1707.25	-60.69
4	M_4 (O3*-O4'**)	-1655.57	-9.01
5	M_5 (O20*-O5'**)	-1790.87	-144.31
6	M_6 (O4*-O5'**)	-1659.89	-13.33
7	M_7 (O3*-O5'**)	-1621.20	25.36
8	M_8 (O21*-O5'**)	-1599.12	47.44
9	M_9 (O20*-O3'**)	-1773.95	-127.39
10	M_{10} (O21*-O3'**)	-1773.95	-127.39
11	M_{11} (O3*-O3'**)	-1816.59	-170.03
12	M_{12} (O21*-O3'**)	-1802.68	-156.12
13	M_{13} (O20*-O3'**)	-1802.68	-156.12
14	M_{14} (O3*-O3'**)	-1802.68	-156.12
15	B_1 (O4'*-O20**, O5'*-O21**)	-1597.74	-5.49
16	B_2 (O4'*-O20**, O5'*-O3**)	-1776.10	-183.85
17	B_3 (O4'*-O20**, O5'*-O4**)	-1601.82	-9.57
18	B_4 (O4'*-O14**, O5'*-O20**)	-1685.99	-93.74
19	B_5 (O4'*-O4**, O5'*-O21**)	-1707.42	-115.17
20	B_6 (O4'*-O4**, O5'*-O3**)	-1757.06	-164.81
21	B_7 (O4'*-O21**, O5'*-O20**)	-1775.64	-183.39
22	B_8 (O4'*-O21**, O5'*-O4**)	-1700.47	-108.22
23	B_9 (O4'*-O21**, O5'*-O3**)	-1639.16	-46.91
24	B_{10} (O4'*-O3**, O5'*-O21**)	-1715.34	-123.09
25	B_{11} (O4'*-O3**, O5'*-O20**)	-1758.79	-166.54
26	B_{12} (O4'*-O3**, O5'*-O4**)	-1738.28	-146.03
27	B_{13} (O5'*-O20**, O3'*-O21**)	-1628.54	-36.29
28	B_{14} (O4'*-O21**, O3'*-O20**)	-1702.70	-110.45
29	B_{15} (O4'*-O21**, O3'*-O4**)	-1849.72	-257.47
30	B_{16} (O5'*-O20**, O3'*-O4**)	-1696.49	-104.24
31	B_{17} (O4'*-O20**, O3'*-O21**)	-1769.41	-177.16
32	B_{18} (O4'*-O20**, O3'*-O4**)	-1720.99	-128.74
33	B_{19} (O5'*-O21**, O3'*-O20**)	-1610.2	-17.95
34	B_{20} (O5'*-O21**, O3'*-O4**)	-1752.34	-160.09
35	T_1 (O4'*-O20**, O5'*-O21**, O3'*-O4**)	-1674.68	-136.74
36	T_2 (O4'*-O20**, O5'*-O4**, O3'*-O3**)	-1511.98	25.96
37	T_3 (O4'*-O4**, O5'*-O21**, O3'*-O20**)	-1600.47	-62.53
38	T_4 (O4'*-O4**, O5'*-O21**, O3'*-O3**)	-1472.14	65.80
39	T_5 (O4'*-O3**, O5'*-O21**, O3'*-O20**)	-1638.56	-100.62
40	T_6 (O4'*-O3**, O5'*-O21**, O3'*-O4**)	-1778.62	-240.68
41	T_7 (O4'*-O21**, O5'*-O20**, O3'*-O4**)	-1695.04	-157.10
42	T_8 (O4'*-O4**, O5'*-O20**, O3'*-O21**)	-1674.98	-137.04
43	T_9 (O4'*-O21**, O3'*-O20**, O5'*-O3**)	-1645.73	-107.79
44	T_{10} (O4'*-O4**, O5'*-O20**, O3'*-O3**)	-1755.28	-217.34
45	T_{11} (O4'*-O3**, O5'*-O20**, O3'*-O21**)	-1537.4	0.54
46	T_{12} (O4'*-O3**, O5'*-O20**, O3'*-O4**)	-1729.12	-191.18
47	T_{13} (O4'*-O21**, O5'*-O4**, O3'*-O20**)	-1681.93	-143.99
48	T_{14} (O4'*-O21**, O5'*-O4**, O3'*-O3**)	-1709.71	-171.77
49	T_{15} (O4'*-O21**, O5'*-O3**, O3'*-O20**)	-1746.99	-209.05
50	T_{16} (O4'*-O20**, O5'*-O4**, O3'*-O21**)	-1674.98	-137.04
51	T_{17} (O4'*-O20**, O5'*-O3**, O3'*-O21**)	-1774.54	-236.60
52	T_{18} (O4'*-O4**, O5'*-O3**, O3'*-O21**)	-1780.56	-242.62
53	T_{19} (O4'*-O3**, O5'*-O4**, O3'*-O20**)	-1658.79	-120.85
54	T_{20} (O4'*-O3**, O3'*-O21**, O5'*-O4**)	-1658.79	-120.85
55	T_{21} (O4'*-O20**, O5'*-O3**, O3'*-O4**)	-1774.54	-236.60
56	T_{22} (O4'*-O4**, O5'*-O3**, O3'*-O20**)	-1780.56	-242.62

** positions of oxygen atoms of hydrated titanium oxide (see figure 1) involved in the hybrid construction*
*** positions of oxygen atoms of benzyl phosphonic acid (see figure 1) involved in the hybrid construction*

3. Results and discussion

From the reaction enthalpies of each hybrid calculated at 298 K (see table 1) hybrid M_{11} had the highest negative value of the reaction enthalpy-with respect to the monodentate hybrids, hybrid B_{15}-with respect to the bidentate hybrids and T_{18}-with respect to the tridentate hybrids.

The heats of reaction of the minimum energy structures thus obtained were calculated at different temperatures, in the range from 298 until 400 K, by the MOPAC 2007 program [5]. Fig. 2 presents the dependence of the heat of reaction versus temperature for the most stable B_{15} hybrid. Low temperatures favor the hybrid formation, similarly to [4].

The negative values of the heat of formation at 298 K of most hybrids point out the possibility of formation of all the three types of considered hybrids, with highest probability of bidentate hybrid formation and the lower probability of tridentate hybrid formation.

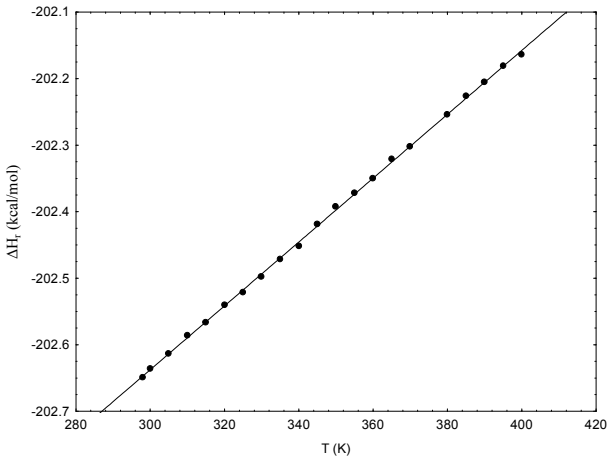


Fig. 2. Dependence of the enthalpy of reaction versus temperature for hybrid B_{15}.

4. Conclusions

Hybrid formation by the benzyl phosphonic acid grafting on titanium oxide was simulated by the semiempirical PM6 method. Starting from a fragment of titanium oxide structure (built from experimental X-ray data) three types of hybrids: monodentate, bidentate and tridentate were considered. The hybrids were energy minimized by the semiempirical PM6 method in vacuum at 298 K. The reaction enthalpies at 298 K were calculated from the formation enthalpies thus obtained. These values indicated the highest probability of B_{15} bidentate hybrid formation. Reaction enthalpies in the range of temperatures from 298 K to 400 K for the most stable hybrid were further calculated. It was observed that lower temperatures favor the bidentate hybrid formation.

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