27 July 2001

ELSEVIER

Chemical Physics Letters 343 (2001) 178–184

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Reactions of titanium oxides with water molecules. A matrix isolation FTIR and density functional study

Limin Shao, Luning Zhang, Mohua Chen, Hao Lu, Mingfei Zhou *

Department of Chemistry and Laser Chemistry Institute, Fudan University, Shanghai 200433, China

Received 7 May 2001; in final form 30 May 2001

Abstract

Reactions of titanium dioxides with water molecules have been studied by matrix isolation infrared and density functional theoretical calculations. In solid argon, titanium dioxide molecules reacted with water to form $OTi(OH)_2$ molecules spontaneously on annealing. The potential energy surface along the $TiO_2 + H_2O \rightarrow OTi(OH)_2$ reaction path was calculated. Although titanium dioxide–water complex was predicted to be stable, this complex was not observed due to low energy barrier and high exothermicity for the hydrolysis reaction. Evidence is also presented for the formation of $OTi–OH_2$ complex. © 2001 Published by Elsevier Science B.V.

1. Introduction

The interaction of water with titanium dioxide is of fundamental importance in a wide variety of fields such as heterogeneous catalysis and photocatalysis, corrosion science and environmental and geochemistry. Supported titanium oxide is currently intensively studied as photocatalyst in water cleavage and decontamination. TiO_2 is also widely used as a pigment in paints and as a catalyst support [1,2]. Accordingly, water adsorption on titanium oxide surface has been well studied both experimentally and theoretically [3].

Recently, water adsorption and hydrolysis on molecular transition metal oxides (TiO_2 and CrO_3) and oxyhydroxides (ScO(OH), $VO_2(OH)$ and $MnO_3(OH)$) has been studied by means of quantum chemistry [4,5]. In the investigated reactions, each reaction step comprised the breaking of one M=O bond and the formation of two OH groups. The reactions were found to involve stable water complexes as intermediates. As far as we know, there is no experimental report on reactions between water and molecular transition metal oxides. In the present study, we report a matrix isolation FTIR spectroscopic and density functional theoretical study on reactions between titanium dioxide molecules and water molecules.

2. Experimental and theoretical methods

The experimental setup for pulsed laser ablation and matrix infrared spectroscopic investigation has been described previously [6]. The 1064 nm Nd:YAG laser fundamental (Spectra Physics, DCR 150, 20 Hz repetition rate and 8 ns pulse width) was focused onto the rotating TiO_2 or Ti targets, and the ablated species were co-deposited with H_2O or O_2/H_2O mixtures in excess argon

---

* Corresponding author. Fax: +86-21-65102777.
E-mail address: mfzhou@fudan.edu.cn (M. Zhou).

0009-2614/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0009-2614(01)00675-3

onto a 11 K CsI window, which was mounted on a cold tip of a closed-cycle helium refrigerator (Air Products, Model CSW202) for 1 h at a rate of 2–4 mmol/h. Typically, 5–10 mJ/pulse laser power was used. H_2O and D_2O were subjected to several freeze–pump–thaw cycles before use. O_2 (Shanghai BOC, 99.6%) and $^{18}O_2$ (Isotec Inc., >97%) were used without further purification. Infrared spectra were recorded on a Bruker IFS113V spectrometer at 0.5 cm^{-1} resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis using a high pressure mercury lamp.

Quantum chemical calculations were performed using the GAUSSIAN 98 program [7]. The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang and Parr was utilized (B3LYP) [8,9]. The 6-311++G(d,p) basis sets were used for H and O atoms, the all electron basis set of Wachters–Hay as modified by Gaussian was used for Ti atom [10,11]. Reactants, various possible transition states, intermediates and products were optimized. The vibrational frequencies were calculated with analytic second derivatives, and zero point vibrational energies (ZPVE) were derived. Transition state optimizations were done with the synchronous transit-guided quasi-Newton(STQN) method [12], followed by the vibrational frequency calculations showing the obtained structures to be true saddle points.

3. Results and discussion

Laser ablation of a bulk TiO_2 target in pure argon produced TiO_2 (946.8, 917.0 cm^{-1}) and TiO (990.2 cm^{-1}) as the major products [13]. When laser-ablated TiO_2 was co-deposited with 0.25% H_2O in argon, new product absorptions at 996.6, 753.6, 677.0, 483.2 and 414.9 cm^{-1} were produced on sample annealing. These absorptions also increased on broadband photolysis and on subsequent 30 K annealing.

Experiments were also done using metal Ti as target and $H_2O + O_2$ mixtures in excess argon as reagent gas, and the representative spectra in the 1010–900 and 770–400 cm^{-1} regions are shown in Fig. 1, with the product absorptions listed in Table 1. Co-deposition of laser-ablated Ti atoms with $H_2O/O_2/Ar$ produced strong TiO_2, O_4^- (953.8 cm^{-1}) [14,15] and very weak TiO absorptions. New absorptions at 996.6, 753.6, 677.0, 483.2 and 414.9 cm^{-1} were observed on annealing as with the $TiO_2 + H_2O/Ar$ experiments. Very weak absorptions due to $Ti + H_2O$ reaction were also observed on broadband photolysis [16]. In the spectra using a $H_2{}^{16}O + {}^{18}O_2$ sample, the TiO_2, TiO and $O_4{}^-$ absorptions were shifted as observed before [13], and the 996.6, 753.6, 677.0, 483.2 and 414.9 cm^{-1} were shifted to 955.5, 745.1, 659.1, 480.9 and 414.3 cm^{-1}, respectively. When a $D_2O + {}^{16}O_2$ sample (with about 40% HDO contamination) was used, the 996.6 cm^{-1} band went to 995.2 cm^{-1}, and both the 753.6 and 677.0 cm^{-1} bands split into two bands at 747.8, 740.6 cm^{-1} and 671.0, 666.9 cm^{-1}, as shown in Fig. 2.

The 996.6, 753.6, 677.0, 483.2 and 414.9 cm^{-1} bands are assigned to different modes of the $OTi(OH)_2$ molecule. These bands were observed in both $TiO_2 + H_2O/Ar$ and $Ti + H_2O/O_2/Ar$ experiments, and increased together on annealing and photolysis, suggesting different vibrational modes of the same molecule. The 996.6 cm^{-1} band showed very small deuterium isotopic shift (about 1.4 cm^{-1}). This band split into two bands at 955.5

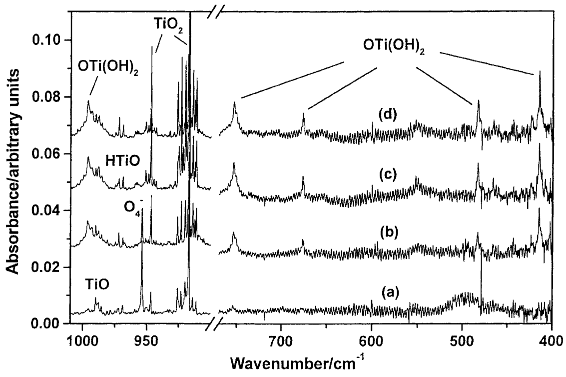


Fig. 1. Infrared spectra in the 1010–900 and 770–400 cm^{-1} regions from co-deposition of laser-ablated Ti atoms with 0.2% $H_2O + 0.5\%\ O_2$ in argon. (a) 1 h sample deposition at 11 K, (b) after 28 K annealing, (c) after 20 min broadband photolysis, and (d) after 30 K annealing.

Table 1
Infrared absorptions (cm^{-1}) from co-deposition of laser-ablated titanium atoms with $H_2O + O_2$ mixtures or laser-ablated TiO_2 with H_2O in excess argon

$H_2{}^{16}O/{}^{16}O_2$	$H_2{}^{16}O/{}^{18}O_2$	$D_2{}^{16}O/{}^{16}O_2$	Assignment
1010.5	1010.5		H_2TiO (Ti=O stretching)
996.6	955.5	995.2	$OTi(OH)_2$ (Ti=O stretching)
990.2	948.3	990.2	TiO
985.7	944.1	985.7	TiO site
968.8	968.8		HTiO (Ti=O stretching)
961.8			$OTi–OH_2$ (Ti=O stretching)
953.8	901.8	953.8	O_4^-
946.8	904.3	946.8	TiO_2 (sym-OTiO stretching)
917.0	881.6	917.0	TiO_2 (asy-OTiO stretching)
753.6	745.1	740.6	$OTi(OH)_2$ (asym-TiOH stretching)
677.0	659.1	666.9	$OTi(OH)_2$ (sym-TiOH stretching)
483.2	480.9		$OTi(OH)_2$ (out-of-plane TiOH bending)
414.9	414.3		$OTi(OH)_2$ (in-plane TiOH bending)

and 951.5 cm^{-1} in the $Ti/H_2{}^{16}O + {}^{18}O_2/Ar$ spectra. The 955.5 cm^{-1} band is the isotopic counterpart, which gave an isotopic $^{16}O/ {}^{18}O$ ratio of 1.043. This ratio is slightly lower than the diatomic TiO ratio 1.0446, indicating that this band is mainly due to a Ti–O stretching vibration. The 951.5 cm^{-1} band is unusually strong, and is mostly due to the overtone of the out-of-plane TiOH bending vibration observed at 480.9 cm^{-1} in Fermi resonance with the 955.5 cm^{-1} band. In the $H_2{}^{16}O + {}^{16}O_2$ case, the 996.6 cm^{-1} Ti–O fundamental is above the overtone by about 30.2 cm^{-1}, and the interaction is diminished. The 753.6 and 677.0 cm^{-1} bands are antisymmetric and symmetric Ti–OH stretching vibrations. In the $H_2{}^{16}O + {}^{18}O_2$ experiment, these two bands shifted to 745.1 and 659.1 cm^{-1}, which correlate to the $^{18}OTi({}^{16}OH)({}^{18}OH)$ molecular absorptions. In the $HDO + D_2O + O_2$ experiments, both the 753.6 and 677.0 cm^{-1} bands split into doublet at 747.8 and 740.6 cm^{-1}, and 671.0 and 666.9 cm^{-1}. These four absorptions are due to antisymmetric and symmetric Ti–OH stretching vibrations of the OTi(OH)(OD) and $OTi(OD)_2$ molecules, respectively. The 483.2 cm^{-1} band shifted to 480.9 cm^{-1} with $H_2{}^{16}O + {}^{18}O_2$, and is assigned to the out-of-plane TiOH bending vibration. The 414.9 cm^{-1} band is probably due to the in-plane TiOH bending vibration.

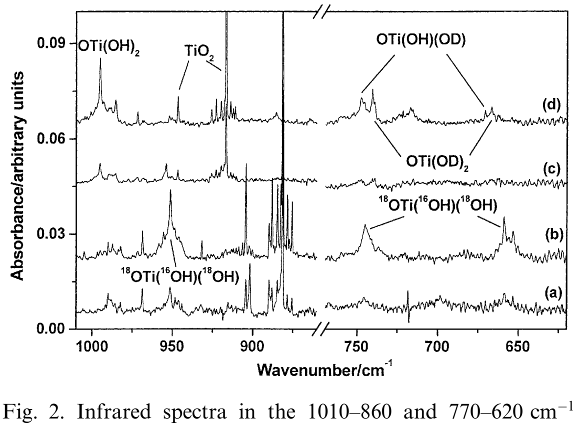
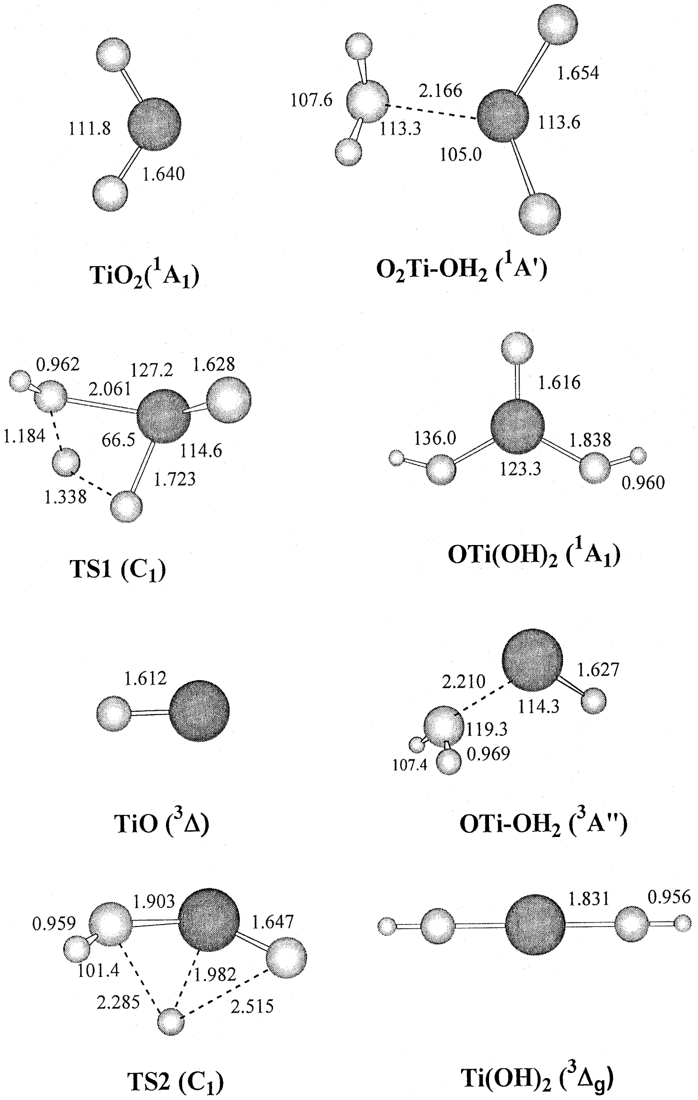


Fig. 2. Infrared spectra in the 1010–860 and 770–620 cm^{-1} regions from co-deposition of laser-ablated Ti atoms with $H_2O + O_2$ mixtures in excess argon. (a) $H_2{}^{16}O + {}^{18}O_2$, sample deposition, (b) after 28 K annealing of sample (a), (c) $HDO + D_2O + O_2$, sample deposition, and (d) after 28 K annealing of sample (c).

DFT calculations support the above assignments. As shown in Fig. 3, the $OTi(OH)_2$ molecule was predicted to have a $^1A_1$ ground state with planar C_{2v} symmetry. The calculated vibrational fundaments are listed in Table 2. The above characterized Ti–O, Ti–OH stretching and bending vibrations were calculated at 1055.2 cm^{-1} (291 km/mol), 784.3 cm^{-1} (282 km/mol), 678.6 cm^{-1} (61 km/mol), 537.8 cm^{-1} (349 km/mol) and 460.1 cm^{-1} (190 km/mol). As can be seen in Table 2, the calculated isotopic frequencies are also in good agreement with the observed values.

Weak absorptions at 961.8 cm^{-1} in the $TiO_2 + H_2O/Ar$ experiments produced on annealing and



$TiO_2(^1A_1)$ $O_2Ti\text{-}OH_2$ ($^1A'$)

TS1 (C_1) $OTi(OH)_2$ ($^1A_1$)

TiO ($^3\Delta$) $OTi\text{-}OH_2$ ($^3A''$)

TS2 (C_1) $Ti(OH)_2$ ($^3\Delta_g$)

Fig. 3. Optimized geometric parameters for TiO, TiO_2, $O_2Ti–OH_2$, $OTi(OH)_2$, $OTi–OH_2$, $Ti(OH)_2$ and transition states (TS1, TS2).

were diminished on broadband photolysis, and were tentatively assigned to the Ti–O stretching vibration of the $OTi–OH_2$ complex. This complex absorption was not observed in the $Ti + H_2O + O_2/Ar$ experiments, as the TiO absorption in these experiments is very weak. As shown in Fig. 3, DFT calculations predicted the $OTi–OH_2$ complex to have a $^3A''$ ground state that correlates to $^3\Delta$ ground state TiO. The Ti–O stretching vibration was calculated at 1009.3 cm^{-1}, red-shifted by about 33.4 cm^{-1} compared with the diatomic TiO vibration calculated at 1042.7 cm^{-1}. Experimentally, we observed a 28.4 cm^{-1} red-shift.

In both the $TiO_2 + H_2O/Ar$ and $Ti + H_2O+ O_2/Ar$ experiments, the primary products after sample deposition are TiO_2 and TiO. The $OTi(OH)_2$ absorptions increased on annealing, indicating that the $OTi(OH)_2$ molecules are formed by reaction of TiO_2 with water in solid argon, reaction (1). This reaction was predicted to be exothermic by about 70.9 kcal/mol at the B3LYP/6-311++G(d,p) level of theory. The

Table 2
Calculated vibrational frequencies (cm^{-1}), and intensities (km/mol) for the structures described in Fig. 3

Molecule	Frequency (intensity, mode)
TiO	1042.7(220)
TiO_2	1026.1(39, a_1), 978.9(470, b_2), 339.7(15, a_1)
$O_2Ti–OH_2$	3869.9(167, a″), 3783.4(a′), 1634.1(114, a′), 1001.2(55, a′), 966.8(488, a″), 554.1(1, a″), 466.9(263, a′), 388.4(52, a′), 305.2(10, a′), 259.1(46, a″), 106.7(133, a′), 77.7(0.1, a″)
$^{16}OTi(^{16}OH)_2$	3907.5(1, a_1), 3904.3(329, b_2), 1055.2(291, a_1), 784.3(282, b_2), 678.6(61, a_1), 537.8(349, b_1), 515.1(0, a_2), 474.0(72, b_2), 460.1(190, a_1), 225.0(19, b_2), 192.8(3, a_1), 53.3(30, b_1)
$^{18}OTi\ (^{16}OH)(^{18}OH)$	3906.1(127), 3892.7(197), 1011.6(279), 774.4(269), 659.5(53), 535.4(340), 512.9(2), 469.2(79), 457.4(186), 217.1(17), 188.5(3), 52.6(29)
$^{16}OTi(^{16}OD)_2$	2846.7(2), 2843.4(225), 1055.1(288), 766.5(309), 666.9(81), 414.2(244), 389.9(23), 388.6(0), 351.9(94), 202.6(20), 178.0(5), 49.6(26)
$OTi–OH_2$	3794.5(87, a′), 3695.6(185, a″), 1611.6(178, a′), 1009.3(285, a′), 442.6(8, a″), 338.9(70, a′), 307.1(74, a′), 96.0(31, a′), 31.6(3, a″)
$Ti(OH)_2$	3973.4(0, σ_g), 3971.3(379, σ_μ), 762.2(357, σ_μ), 649.9(0, σ_g), 457.6(404, π_μ), 454.0(0, π_g), 40.5(10, π_μ)
TS1	3878.0(113), 1893.8(78), 1263.9(71), 1030.7(287), 910.6(267), 662.0(97), 605.2(99), 501.4(126), 409.5(147), 277.8(33), 116.2(46), 1393.1i(1659)
TS2	3926.0(138), 973.4(157), 829.2(138), 622.4(77), 466.6(130), 430.4(146), 241.0(58), 143.6(23), 443.0i(31)

$OTi(OH)_2$ absorptions increased on annealing also suggest that reaction (1) requires negligible activation energy.

$$TiO_2(^1A_1) + H_2O(^1A_1) \rightarrow OTi(OH)_2(^1A_1), \quad \Delta E = -70.9\ \text{kcal/mol}. \qquad (1)$$

The reactions of water with TiO_2 molecules were recently addressed by Johnson and Panas by using density functional calculations [4]. We have also calculated the potential energy surface along the $TiO_2 + H_2O \rightarrow OTi(OH)_2$ reaction path, and the result is shown in Fig. 4. Our calculation results are in good agreement with those of Johnson and Panas. Water reacts with TiO_2 to form a stable $O_2Ti–OH_2$ complex. Formation of this complex was predicted to be exothermic by 28.0 kcal/mol,

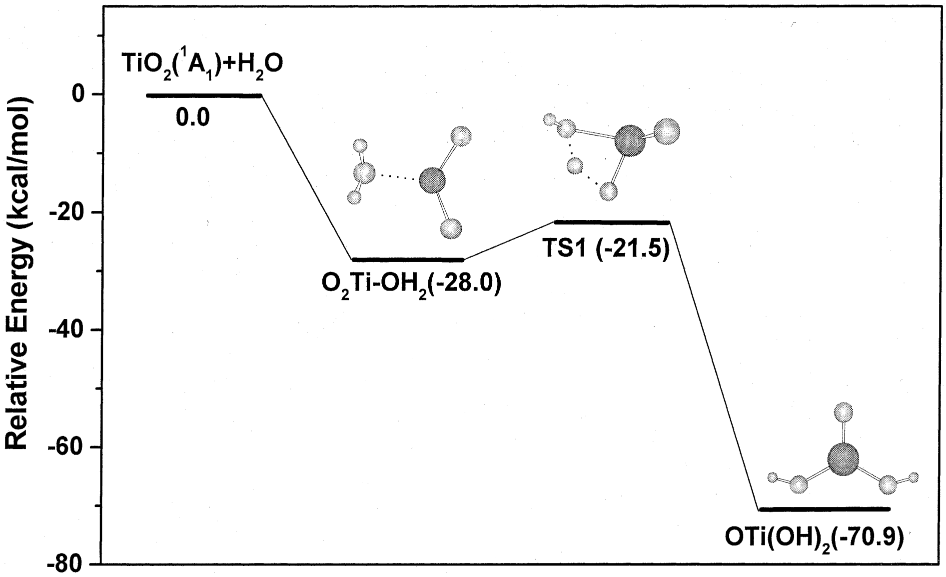


Fig. 4. Potential energy surface along the $TiO_2 + H_2O \rightarrow OTi(OH)_2$ reaction path. Energies given are in kcal/mol and are relative to the ground state reactants: $TiO_2(^1A_1) + H_2O(^1A_1)$.

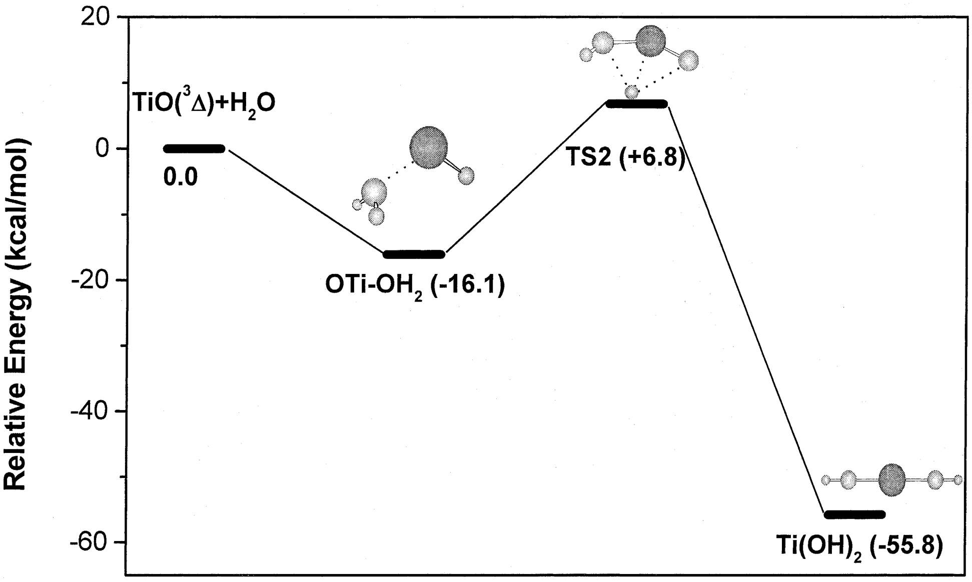


Fig. 5. Potential energy surface along the TiO + $H_2O \rightarrow Ti(OH)_2$ reaction path. Energies given are in kcal/mol and are relative to the ground state reactants: $TiO(^3\Delta) + H_2O(^1A_1)$.

and is barrier-free. The complex has non-planar C_s symmetry with coordination between Ti atom and O atom of the H_2O unit. As can be seen from Table 2, the antisymmetric and symmetric TiO_2 stretching vibrations were predicted to be red-shifted by about 12.1 and 24.9 cm^{-1} compared with those of TiO_2. No evidence was found for this complex in present experimental conditions.

In O_2Ti–OH_2 complex, a hydrogen atom could transfer to one of the O atoms in the TiO_2 unit to form the $OTi(OH)_2$ molecule through a transition state. The geometric parameters of this transition state are also shown in Fig. 3. The hydrolysis reaction from O_2Ti–OH_2 to $OTi(OH)_2$ was exothermic by about 42.9 kcal/mol, with an energy barrier of 6.5 kcal/mol. As the water addition to TiO_2 is initially exothermic by 28.0 kcal/mol, which significantly surmounts the energy barrier for the hydrolysis reaction, the formation of $OTi(OH)_2$ is spontaneous in solid argon, as evidenced by the increase of the $OTi(OH)_2$ absorptions on annealing. This also suggests that the O_2Ti–OH_2 complex is very short-lived, rapidly rearranging to form the $OTi(OH)_2$ molecule.

According to Johnson and Panas's calculations [4], the $OTi(OH)_2$ molecule could further react with water molecule to form $OTi(OH)_2$–H_2O complex and finally to $Ti(OH)_4$. Note that the $OTi(OH)_2$ absorptions are weak in present experimental conditions, the subsequent reaction products probably are too weak to be observed.

In the $TiO_2 + H_2O/Ar$ experiments, laser ablation of the TiO_2 target also produced substantial TiO molecules, and the OTi–OH_2 complex was formed via reaction (2):

$$TiO(^3\Delta) + H_2O(^1A_1) \rightarrow OTi\text{–}OH_2(^3A''), \quad \Delta E = -16.1\ \text{kcal/mol}. \tag{2}$$

This reaction is exothermic by about 16.1 kcal/mol. One could imagine the formation of $Ti(OH)_2$ from OTi–OH_2 analogous to the O_2Ti–OH_2 reaction. However, no evidence was found for the formation of the $Ti(OH)_2$ molecule. Fig. 5 shows the potential energy surface along the TiO + $H_2O \rightarrow Ti(OH)_2$ reaction path. The hydrolysis reaction from OTi–OH_2 to $Ti(OH)_2$ has an energy barrier of 22.9 kcal/mol, significantly higher than the energy barrier for the TiO_2 hydrolysis reaction. The transition state is even higher than the separated reactants $TiO(^3\Delta) + H_2O$ by about 6.8 kcal/mol.

4. Conclusions

Laser-ablated Ti atoms co-deposited with $H_2O + O_2$ mixtures in excess argon to form titanium dioxide as the primary product. The $OTi(OH)_2$ molecules were produced spontaneously on annealing via reactions between TiO_2 and H_2O. The $OTi(OH)_2$ molecule was identified by isotopic substitutions as well as density functional calculations. The potential energy surface along the $TiO_2 + H_2O \rightarrow OTi(OH)_2$ reaction path was calculated. The calculation results showed that the first step for this reaction is the formation of an $O_2Ti–OH_2$ complex. Although this complex was predicted to be stable, it was not observed due to low energy barrier and high exothermicity for the subsequent hydrolysis reaction. Experiments with a TiO_2 target and using H_2O/Ar as reagent gas also produced the $OTi(OH)_2$ molecules.

Acknowledgements

We greatly acknowledge support for this research from NSFC (Grant No. 20003003).

References

[1] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.
[2] R.L. Pozzo, M.A. Baltanas, A.E. Cassano, Catalysis Today 39 (1997) 219.
[3] G.E. Grown, V.E. Henrich, W.H. Lasey, et al., Chem. Rev. 99 (1999) 77.
[4] J.R.T. Johnson, I. Panas, Inorg. Chem. 39 (2000) 3192.
[5] J.R.T. Johnson, I. Panas, Inorg. Chem. 39 (2000) 3181.
[6] M.H. Chen, X.F. Wang, L.N. Zhang, M. Yu, Q.Z. Qin, Chem. Phys. 242 (1999) 81.
[7] M.J. Frisch, G.W. Trucks, et al., GAUSSIAN 98 Revision A.7; Gaussian, Inc., Pittsburgh, PA, 1998.
[8] C. Lee, E. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[9] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[10] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639.
[11] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
[12] M. Head-Gordon, J.A. Pople, M. Frisch, Chem. Phys. Lett. 153 (1988) 503.
[13] G.V. Chertihin, L. Andrews, J. Phys. Chem. 99 (1995) 6356, and references therein.
[14] M.E. Jacox, W.E. Thompson, J. Chem. Phys. 100 (1994) 750.
[15] M.F. Zhou, J. Hacaloglu, L. Andrews, J. Chem. Phys. 110 (1999) 9450.
[16] M.F. Zhou, L.N. Zhang, J. Dong, Q.Z. Qin, J. Am. Chem. Soc. 122 (2000) 10680.