Temperature Programmed Desorption Study of Water Adsorbed on Metal Oxides. I. Anatase and Rutile

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The adsorbed state of water on TiO_2 was studied by temperature programmed desorption (TPD) in the range 0—1000 °C. Pure anatase and rutile samples, the TPD spectra of water from which were not affected by any contaminant, could be obtained by the hydrolysis of titanium oxalate and tetrachloride solutions, respectively. Two desorption peaks were observed for anatase with the peak maxima at 69—127 (I) and 191—256 °C (II), and three for rutile at 32—90 (I), 188—265 (II), and 310—356 °C (III). The sum of adsorbed amounts for peaks II, and III are within a monolayer coverage, that of peak I exceeding it. The enthalpies of adsorption were evaluated to be 36 and 55—69 $kJ \cdot mol^{-1}$ for peaks I and II of anatase, and 36, 64, and 104 $kJ \cdot mol^{-1}$ for peaks I, II, and III of rutile, respectively. From these results, the corresponding adsorbed species of peak I was tentatively assigned to physical adsorption, that of peak II to chemisorption on surface oxygen ion by hydrogen bond, and that of peak III to chemisortpion on Ti^{4+} by the coordination of oxygen atom of water molecule. The last species may be dissociated into surface OH groups.

Most metal oxides are covered with hydroxyl groups under normal conditions.[1] Since surface hydroxyl groups seem to have a great influence on the physical and chemical properties of metal oxide surface, it is important to have information on the adsorbed state of water on the surface.

The adsorbed state of water on titanium dioxide has been investigated by many authors by various methods: specific chemical reactions,[1] adsorption measurement,[2] infrared spectroscopy,[3] and temperature programmed desorption spectroscopy.[4-6] However, many problems remain unsolved: (1) whether surface hydroxyl groups are isolated freely or associated with each other through hydrogen bond, (2) whether there exists molecular species adsorbed by chemical or physical cohesion bond besides surface hydroxyl groups, (3) the amount and the adsorption bond strength of each adsorbed species, and (4) the difference between anatase and rutile. In the present work, these subjects were studied in detail by the temperature programmed desorption (TPD) technique.

Experimental

Materials. The crystal form of titanium dioxide prepared by the hydrolysis of titanium salts depends on the sort of electrolyte in the solution and on the calcination temperature.[7-9] Rutile is usually obtained by calcination above 900 °C. The rutile sample thus obtained, however, is not adequate for studying the surface phenomena because of its small surface area. In the present work, three kinds of anatase (A-1—3) and two kinds of rutile (R-1,2) samples were used (Table 1). Sample A-1 is of extra pure grade (Wako Pure Chemical Industries, Ltd.). Sample A-2 was prepared from titanium sulfate obtained by the reaction of titanium dioxide with concd H_2SO_4. The titanium sulfate solution was hydrolyzed with ammonia. The precipitate was washed with distilled water to remove sulfate ions thoroughly, and dissolved in an aqueous solution of oxalic acid. The hydrolysis of the titanium oxalate solution was then repeated twice with ammonia. Finally the washed precipitate was dried at 120 °C, and calcined at 600 °C in the air for 5 h. Sample A-3 was obtained by the hydrolysis of a titanium tetrachloride solution with ammonia in the presence of ammonium sulfate, followed by thorough washing, drying at 120 °C, and then calcination at 730 °C in the air for 3 h.

The hydrolysis of a titanium tetrachloride solution in the absence of ammonium sulfate gave rise to the formation of rutile crystals by calcination at 600 °C (the sample is denoted by R-1). Sample R-2 was also obtained by the hydrolysis of titanium tetrachloride, followed by washing with ammonium nitrate solution to improve the filtration yield.

The samples were confirmed by X-ray diffraction analysis to be pure anatase or rutile except sample R-2, which contains a small amount of anatase crystals. The surface areas of the samples were measured by the BET method with nitrogen as an adsorbate. Granules of 20—80 mesh were used for TPD experiments.

Apparatus. The apparatus used for the TPD experiments is essentially the same as that described previously.[10] Equipments added were a path of oxygen for pretreatment under oxygen atmosphere, and a water vapor supplier consisting of a saturated solution of sodium chloride held at 0 or 20 °C. Water vapor was supplied to the sample by passing a carrier gas through the supplier for a certain period. Helium was used as a carrier gas. Commercial helium and oxygen were dried with a phosphorus pentoxide column.

Procedure. A fixed amount of TiO_2 (0.25, 0.5, or 1.0 g) was loaded into the reactor. The sample was heated at 600 °C for 1 h under a stream of mixed gas of oxygen 10% and helium 90% (50 $cm^3 \cdot min^{-1}$) and then under a stream of helium for 1 h. After the sample had been cooled to 0 or 20 °C, the water vapor was supplied and adsorbed from the supplier for a certain period with a helium carrier (50 $cm^3 \cdot min^{-1}$). The partial pressure of water vapor was 0.61 or 2.34 kPa. The water vapor in gas phase was then purged by the helium carrier, programmed heating being started from 0 or 20 to 1000 °C at a constant rate of $b=3.5$—25 $K \cdot min^{-1}$. Gas desorption during the course of heating was recorded as a TPD chromatogram with a conventional thermal conductivity detector. The desorbed species was identified by gas chromatography. The amount of desorbed species was calculated from the peak area of the TPD chromatogram.

Results and Discussion

Desorption Chromatogram. Figure 1 shows the TPD chromatograms from three kinds of anatase sam-

Table 1. TiO_2 Samples used

Sample	Preparation method	Calcination	Surface area/$m^2 \cdot g^{-1}$	X-Ray diffraction
A-1	Commercial TiO_2	600 °C-5 h	6.4	Anatase
A-2	Hydrolysis of $Ti(SO_4)_2$ → dissolve in $(COOH)_2$ → hydrolysis → washed by distd H_2O	600 °C-5 h	34.2	Anatase
A-3	Hydrolysis of $TiCl_4$ in the presence of $(NH_4)_2SO_4$ → washed by distd H_2O	730 °C-3 h	11.2	Anatase
R-1	Hydrolysis of $TiCl_4$ → washed by distd H_2O	600 °C-5 h	14.5	Rutile
R-2	Hydrolysis of $TiCl_4$ → washed by NH_4NO_3 soln	600 °C-5 h	15.4	Rutile (+Anatase)

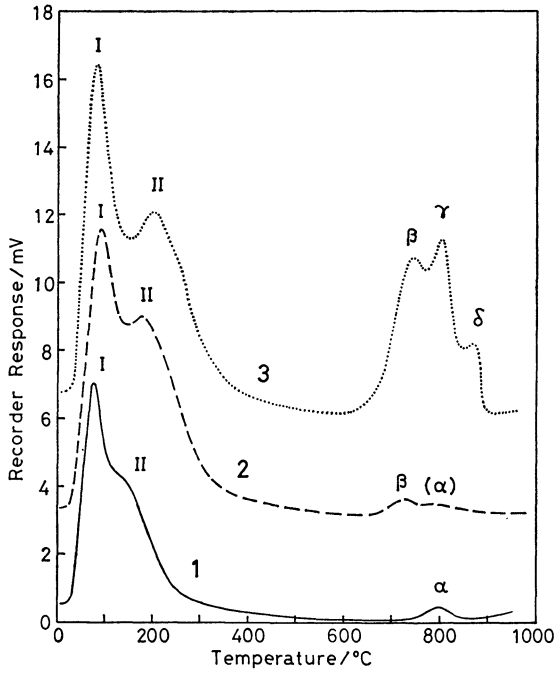


Fig. 1. TPD chromatograms from three anatase samples. Water vapor was fully preadsorbed at 0 °C after pretreated at 600 °C. Heating rate $b=15\ K \cdot min^{-1}$. 1: Sample A-1 1.0 g, 2: sample A-2 0.25 g, 3: sample A-3 0.5 g. For clarity, chromatograms 2 and 3 have been translated by 3 and 6 units along the ordinate, respectively.

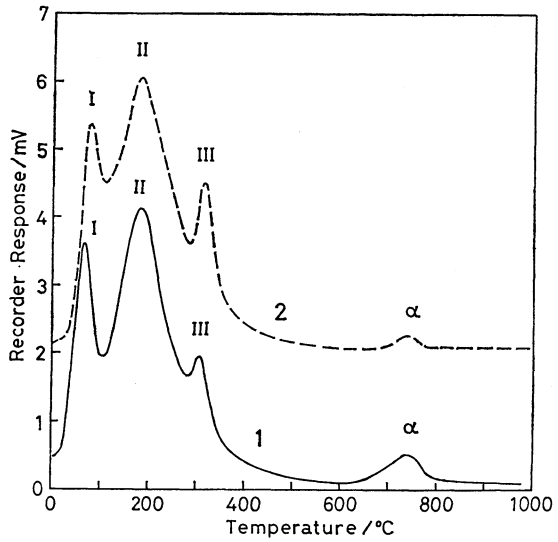


Fig. 2. TPD chromatograms from two rutile samples. Water vapor was fully preadsorbed at 0 °C after pretreated at 600 °C. $b=15\ K \cdot min^{-1}$. 1: Sample R-1 0.5 g, 2: sample R-2 0.5 g. For clarity, the chromatogram 2 has been translated by 2 units along the ordinate.

ples, which were pretreated at 600 °C and then allowed to adsorb water vapor at 0 °C, in the range 0—1000 °C. Similar results obtained from two kinds of rutile samples are shown in Fig. 2. The crystal structure of samples did not change with pretreatment. All samples pretreated showed no desorption peak up to 600 °C unless water was preadsorbed, but above 600 °C the same chromatograms were also observed without the preadsorption of water.

The chromatograms (Figs. 1 and 2) can be divided broadly into two groups; one with desorption peaks below and the other above 600 °C. The desorbed gases at lower temperatures were identified to be water alone by gas chromatography. Two desorption peaks I and II from sample A-2 well correspond to those from sample A-3. In the case of sample A-1, peak II was faintly observed as a shoulder of peak I. Munuera *et al.*[4] also reported two desorption peaks with the peak maxima at 175 and 215 °C. The rutile samples, on the other hand, gave three desorption peaks of water. Lower temperature peaks I and II correspond to those from anatase, no peak III being observed in the latter. The desorption peaks at 250 and 370 °C reported by Munuera and Stone[5,6] seem to be equivalent to peaks II and III (Fig. 2), though the peak temperatures are higher than the present results. Munuera[5] also reported another peak near 500 °C in the first TPD experiment using a fresh rutile sample evacuated at 400 °C, and attributed the peak to free OH groups from the original hydroxide. However, no such peak has been observed in the present work even though the sample was pretreated at 400 °C.

On the other hand, for the desorption peaks above 600 °C the desorbed gases were not water. Gas chromatographic analysis showed that peak α of sample

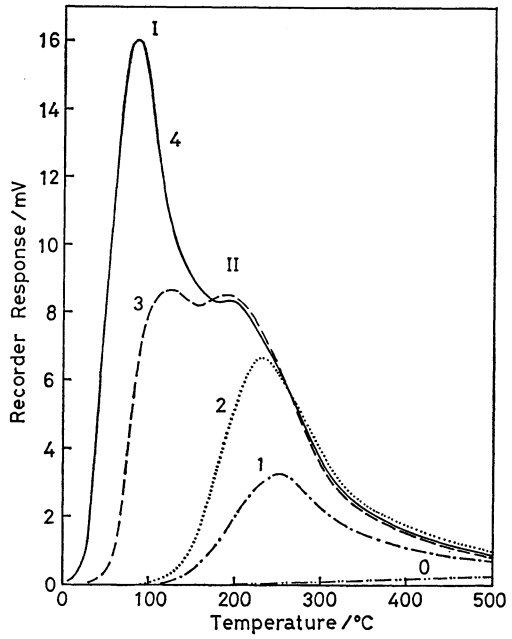


Fig. 3. The change of TPD chromatogram of water from sample A-2 (1.0 g) by the preadsorbed amount V_a of water. V_a value in each run is given in Table 2. $b=15$ K·min^{-1}. Run 0: no adsorption, 1: adsorption for 10 min, 2: 20 min, 3: 40 min, 4: 60 min.

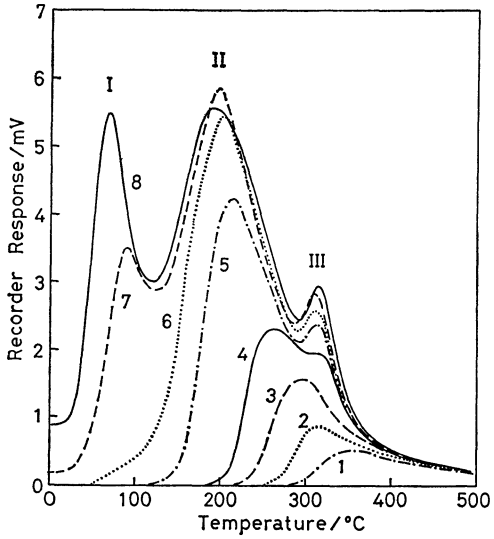


Fig. 4. The change of TPD chromatogram of water from sample R-1 (1.0 g) by the preadsorbed amount V_a of water. V_a value in each run is given in Table 3. $b=10$ K·min^{-1}. Run 1: adsorption for 1 min, 2: 1.5 min, 3: 2.5 min, 4: 4 min, 5: 9 min, 6: 12 min, 7: 15 min, 8: 21 min.

R-1 or R-2 at about 740 °C and peak α of sample A-1 at 800 °C arises from the desorption of surface oxygen. Several types of adsorbed oxygen species have been proposed over various metal oxides such as O_2^-, O^-, and O^{2-}. Peak α could be assigned to O^{2-} species since the former two species should be desorbed up to 600 °C.[10,11] The amount of α oxygen obtained from peak area of sample R-1 was evaluated to be 8.6×10^{-8} mol·m^{-2} of TiO_2 surface, corresponding to the surface coverage of *ca.* 1% with respect to surface titanium atoms. In the case of sample A-2, nitrogen was also detected in addition to oxygen as a desorbed gas. In particular most of peak β was due to the desorption of nitrogen. For large peaks β, γ, and δ from sample A-3 the desorbed gases were not oxygen, but nitrogen and unknown species. Lower calcination temperature caused the enlargement of these peaks as compared with peak II. From the results, it is concluded that the abnormally large, higher temperature peaks should correspond to the desorption with decomposition of ammonium sulfate residue used for preparation. Thus the preparation method of sample A-3 is not appropriate for pure anatase.

In the case of sample A-2, the coverage of impurity can be estimated to be only a few percent since the area of peak β is much smaller than that of peak II which corresponds to the adsorption amount within a monolayer coverage. When sample A-2 was pretreated at 850 °C to remove the impurity the feature of the desorption chromatogram of water was the same as the result in Fig. 1, though the recorder response was very low because of the decreased surface area. Thus, the influence of impurity for sample A-2 is negligible and the spectrum up to 600 °C (Fig. 1) can be taken to represent the desorption chromatogram of water from pure anatase surface.

Peak II of commercial sample A-1 represents a smaller peak area and a lower peak temperature than that of sample A-2. This may be caused by some impurities. Commercial sample is likely to contain some iron compounds or some phosphates.[12] Munuera *et al.*[4] reported that the addition of phosphate ions to anatase results in the disappearance of peak II.

Changes of Desorption Chromatograms by Adsorbed Amounts. Anatase and rutile show different TPD chromatograms; the former has two desorption peaks, the latter three. These peaks should reflect the different types of adsorbed states of water on the different surface sites. In order to obtain further information on the corresponding adsorbed states of these peaks, TPD chromatograms were measured at various amounts of water preadsorbed.

Figure 3 shows the TPD chromatograms from sample A-2 of anatase form after water vapor had been preadsorbed in various amounts at 0 °C. The amount of water preadsorbed was varied by passing helium carrier gas over the saturated solution of sodium chloride held at 0 °C for the periods 0—65 min. When the preadsorbed amount V_a was small, only one peak (II) appeared. With increasing V_a, peak II was enhanced, the peak temperature being lowered. However, the increase of peak II was saturated to a certain limit and another peak I appeared in the lower temperature region at $V_a=11.63$ μmol·m^{-2}. Similar results were also obtained in the case of sample A-1.

Figure 4 shows the results from sample R-1 of rutile form. Only one peak was observed for runs 1, 2, and 3, where the preadsorbed amount was less than 2.43 μmol·m^{-2}. The chromatogram started to separate into two peaks (II and III) at $V_a=3.53$ μmol·m^{-2} (run 4), the peak separation becoming clear by the further adsorption of water. At $V_a=9.08$ μmol·m^{-2}

Table 2. Analysis of TPD chromatograms of water from anatase A-2 sample

Run	V_a [a] / μmol·m^{-2}	Peak I			Peak II		
		T_M [b] / °C	V_d [c] / μmol·m^{-2}	ΔH [d] / kJ·mol^{-1}	T_M [b] / °C	V_d [c] / μmol·m^{-2}	ΔH [d] / kJ·mol^{-1}
1	3.56	—	0	—	256	3.56	—
2	6.75	—	0	—	233	6.75	69
3	11.63	127	3.89	—	191	7.74	—
4	19.58	88	11.99	36	204	7.59	55
5	23.33	69	15.81	—	199	7.52	—

a) Preadsorbed amount, the sum of V_d for peaks I and II. b) Temperature at peak maximum at $b=15$ K·min^{-1}. c) Amount of desorbed H_2O. d) Enthalpy of adsorption.

Table 3. Analysis of TPD chromatograms of water from rutile R-1 sample

Run	V_a [a] / μmol·m^{-2}	Peak I			Peak II			Peak III		
		T_M [b] / °C	V_d [c] / μmol·m^{-2}	ΔH / kJ·mol^{-1}	T_M [b] / °C	V_d / μmol·m^{-2}	ΔH / kJ·mol^{-1}	T_M [b] / °C	V_d / μmol·m^{-2}	ΔH / kJ·mol^{-1}
1	0.97	—	0	—	—	0	—	356	0.97	—
2	1.39	—	0	—	—	0	—	317	1.39	—
3	2.43	—	0	—	overlap					
4	3.53	—	0	—	265	1.59	—	316	1.94	—
5	7.67	—	0	—	212	5.56	—	313	2.11	—
6	9.08	—	0.29	—	203	6.56	—	310	2.23	—
7	12.66	90	2.48	—	197	7.86	—	310	2.32	—
8	13.58	68	3.66	36	190	7.69	64	315	2.23	104
9	17.68	54	7.57	—	188	7.90	—	313	2.21	—
10	25.33	32	15.37	—	191	7.65	—	315	2.31	—

a) Preadsorbed amount, the sum of V_d for peaks I, II, and III. b) At $b=10$ K·min^{-1}.

(run 6), both these peaks almost attained their saturated heights. Peak I appeared at a preadsorbed amount greater than $V_a=12.6$ μmol·m^{-2}. A comparison of peak temperatures suggests that peaks I and II of rutile correspond to two peaks of anatase; peak III is characteristic of rutile form.

Taking into account the long tailing of peak II from anatase, however, it is reasonable to consider that the adsorbed species corresponding to peak III from rutile should exist on the anatase surface. Smaller amount or lower desorption temperature than that of rutile may interfere with the appearance of a discrete peak.

Peak II of anatase and peaks II and III of rutile have attained the saturated adsorption. This indicates that the peaks should arise from the desorption of some species chemisorbed within a surface monolayer. For the sake of confirmation, the amounts of desorbed gas were determined from the peak areas of TPD chromatograms (Figs. 3 and 4). The results are given in Tables 2 and 3, respectively. The temperature at the minimum of chromatogram was taken as the boundary between two peaks. Assuming that every surface oxygen ion with the coordination number less than three is hydroxylated, the maximum amounts of desorbed water from the (100), (001), and (110) planes of anatase are calculated to be 9.28, 11.7, and 13.1 μmol·m^{-2}, respectively. For the (110), (101), and (001) planes of rutile, they amount to 8.64, 9.93, and 15.7 μmol·m^{-2}, respectively.

The maximum values observed for peak II of anatase and for peak II+III of rutile are in good agreement with the calculated values for low index planes. It is concluded that either peak II or III corresponds to chemisorbed species on the surface. On the other hand, the desorbed amount of peak I did not attain a saturated value, but increased over a monolayer coverage (Tables 2 and 3). It might be concluded that peak I corresponds to the physical adsorption species.

The Enthalpy of Adsorption. In order to estimate the adsorption strength of each species, the enthalpy of adsorption ΔH was measured for two peaks of sample A-2 and for three peaks of sample R-1. ΔH was determined according to the method of Konvalinka *et al.*[13] who extended the theory of Cvetanovic and Amenomiya.[14]

For the first order desorption from a homogeneous surface with freely occurring readsorption, peak temperature T_M of a desorption peak is correlated with ΔH and heating rate b by

$$2\log T_M - \log b = \frac{\Delta H}{2.303RT_M} + \log\frac{(1-\theta_M)^2 V_s \Delta H}{FAR}. \quad (1)$$

For second order desorption with freely occurring readsorption, Eq. 1 may be written as

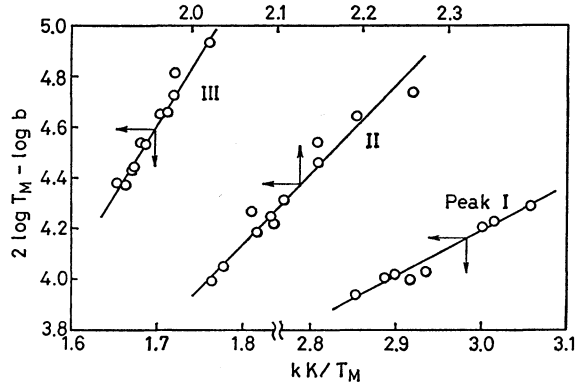


Fig. 5. Plots of (2 log T_M − log b) *vs.* $1/T_M$ for three TPD peaks from sample R-1.

$$2\log T_M - \log b = \frac{\Delta H}{2.303RT_M} + \log\frac{(1-\theta_M)^2 V_s v_m \Delta H}{2\theta_M FAR}, \quad (2)$$

where R is the gas constant, V_s the volume of the solid phase, v_m the amount of gas adsorbed at full coverage per unit volume of the solid in a certain adsorbed state, F the flow rate of carrier gas, θ_M the coverage at $T=T_M$, and A is equal to $\exp(\Delta S/R)$, where ΔS is the entropy of adsorption. The flow rate of carrier gas 50 $cm^3 \cdot min^{-1}$ fulfills the condition with freely occurring readsorption, because desorption without readsorption cannot be realized unless the flow rate is set at 10^7 $cm^3 \cdot h^{-1}$ per gram of solid.[13] Since θ_M varies very slightly with heating rate, the slope of the plot of (2 log T_M −log b) *vs.* $1/T_M$ should provide the enthalpy of adsorption at constant F and at constant initial surface coverage both for the first and second order desorption. Figure 5 shows the plots of (2 log T_M −log b) *vs.* $1/T_M$ for three peaks of sample R-1. In all cases, a linear relation holds. ΔH's calculated from the slopes are also given in Tables 2 and 3.

Day *et al.*[15] reported the values 45—52 $kJ \cdot mol^{-1}$ for the heat of adsorption of water on rutile at 25 °C in the region of monolayer coverage. Morimoto *et al.*[16] obtained the values 79.5 and 105.4 $kJ \cdot mol^{-1}$ for the heats of hydration of rutile and anatase, respectively, from the measurement of heat of immersion in water. The values of Day *et al.* are intermediate between the ΔH values for peaks I and II. The values of Morimoto *et al.* are close to the present result for peak III of rutile, which is in good agreement with the result of Munuera and Stone.[6] However, Day *et al.* and Morimoto *et al.* paid no attention to the difference of adsorbed species. The different species should exhibit a different heat of adsorption or immersion.

Adsorbed State of Water. The ΔH value 36 $kJ \cdot mol^{-1}$ for peak I agrees with the heat of vaporization of water at 100 °C, 41 $kJ \cdot mol^{-1}$. The ΔH values for peak II are in the range 55—69 $kJ \cdot mol^{-1}$, greater than the heat of vaporization. Hydrogen bonds would participate in the adsorption of peak II species. From the fact that peak I arises after peak II has attained saturation, peak II can be assigned to the chemisorbed species held on the surface oxygen ions by hydrogen bond within a monolayer, and peak I to the multilayer physical adsorption on the chemisorbed water molecules. The hydrogen bond of water molecule with surface oxygen ion O^{2-} is considered to be stronger than that between water molecule since O^{2-} ion has a higher proton affinity than the oxygen atom of water molecule.

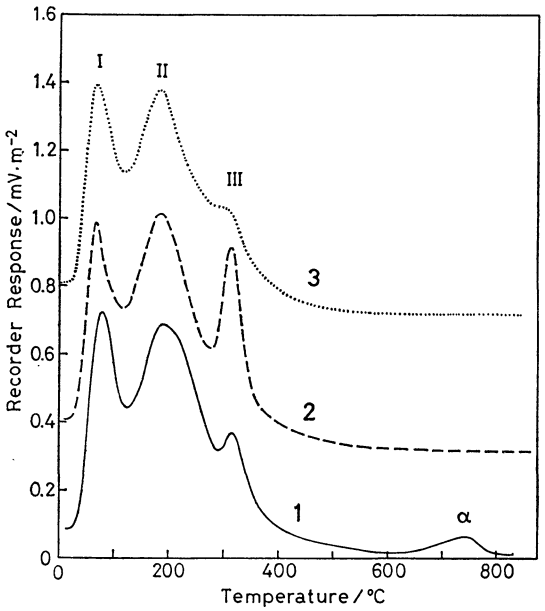


Fig. 6. The influence of pretreatment on the adsorption sites of sample R-1. 1: First run after pretreated at 600 °C, 2: second run after first TPD up to 830 °C, 3: third run after pretreated at 1000 °C for 30 min. Water was fully preadsorbed at 20 °C. $b=10$ K·min^{-1}. For clarity, the chromatograms 2 and 3 have been translated by 0.3 and 0.7 units along the ordinate.

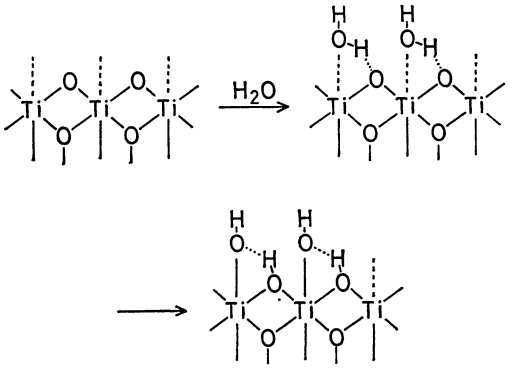
The ΔH value 104 $kJ \cdot mol^{-1}$ for peak III of rutile is considerably greater than that expected for the adsorption through hydrogen bond. On the other hand, it is indicated by infrared study[17] that free OH groups remain on the surface of silica gel or alumina even after evacuation at 650—950 °C. Thus free OH groups are likely to be able to desorb only at very high temperatures. Peak III can be tentatively assigned to the adsorbed species through the coordination of oxygen atom of water to the surface titanium ion.

In order to confirm the participation of Ti^{4+} ions in the peak III adsorption, the following experiments were carried out. After the surface oxygen (peak α) had been desorbed from sample R-1 by the first TPD procedure up to 830 °C (curve 1, Fig. 6), the sample was quenched to 20 °C in a stream of helium. Water was then readsorbed and the TPD chromatogram was recorded again. The result is shown in curve 2, where recorder response was plotted per unit area since the surface area decreased from 14.5 to 5.3 $m^2 \cdot g^{-1}$ by the first TPD run up to 830 °C. The magnitude of peak III markedly increased in the second run, that of peak II remaining almost unchanged. The increase of peak III is probably due to the increase of the number of Ti^{4+} sites by the desorption of surface oxygen ions. Elongated heat treatment above 800 °C caused a gradual decrease in surface area. The sintering

process would bring about the change of surface structure, in particular the decrease of the active Ti^{4+} sites, which results in the reduction of peak III. The result on sample R-1 pretreated at 1000 °C for 30 min, the surface area of which decreased to 1.65 $m^2 \cdot g^{-1}$, is given by curve 3. The reduction of peak III is considerable, but the magnitude of peak II per unit area remains unchanged. The results suggest the participation of Ti^{4+} sites in the adsorption of peak III species; the peak II species seem to be independent of Ti^{4+} sites. The possibility that reduced Ti^{3+} ions might be the peak III adsorption sites can be eliminated since in such a case curve 3, representing the run after pretreatment at the highest temperature in the inert gas, should exhibit the largest peak III.

Similar experiments were carried out on anatase sample A-2, but no clear peak III could be observed by any pretreatment. Thus the sites of Ti^{4+} on anatase are much fewer or weaker than those on rutile. This can be explained as follows. Since the cleavage of anatase crystal along (100), (001), and (110) planes produces 5-coordinate surface Ti^{4+} ions in each case, the oxygen atom of water molecule could be coordinated to only one Ti^{4+} ion at its vacant ligand position. In the case of rutile, a water molecule can be doubly coordinated to two adjacent 4-coordinate Ti^{4+} ions on the (100) and (110) planes. Such adsorption modes may be reflected in the difference of the desorption spectrum of peak III.

Primet *et al.*[3] suggested from infrared spectroscopic study that the surface of anatase and rutile evacuated at 200 or 300 °C for 20 h contains hydroxyl groups, and that OH groups bonded with each other by hydrogen bridges should be removed by evacuation at 350 °C and isolated OH groups at 400 °C. The former OH groups seem to be equivalent to peak III in the present work from the coincidence of desorption temperature. It is likely that a water molecule coordinated to Ti^{4+} ion would form the hydrogen bond with an adjacent surface O^{2-} ion, and dissociate into two OH groups by proton shift through hydrogen bond as follows:



(3)

On the other hand, no desorption of free OH groups was observed as a peak in TPD chromatogram. However, it should be related to the long tailing part of chromatogram which starts at about 350 °C and continues above 600 °C, since the desorbed gas from a long tail was also found to be water. Thus the present results suggest the existence of some free OH groups still above 400 °C, contrary to the suggestion of Primet *et al.*[3]

Conclusion

The TPD chromatogram of water from anatase surface consists of two peaks, (I) T_M=69—127 °C, ΔH=36 kJ·mol^{-1} and (II) T_M=191—250 °C, ΔH=55—69 kJ·mol^{-1}, while that from rutile consists of three peaks, (I) T_M=32—90 °C, ΔH=36 kJ·mol^{-1}, (II) T_M=188—265 °C, ΔH=64 kJ·mol^{-1}, and (III) T_M=310—356 °C, ΔH=104 kJ·mol^{-1}. Peaks I and II from both samples well correspond to each other. Peak II of anatase and peaks II and III of rutile attain saturated adsorption within a surface monolayer coverage. On the other hand, the adsorption of peak I on both samples was not saturated but increased over a monolayer coverage. Three desorption peaks are concluded to correspond to the following adsorbed states.

peak I: Physically adsorbed species on surface hydroxyl groups or chemisorbed water molecules.

peak II: Chemisorbed species on surface oxygen ions through hydrogen bonds.

peak III: Chemisorbed species on Ti^{4+} ions through coordination bond. The species can be transformed into two OH groups by proton transfer to an adjacent surface oxygen ion.

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