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The Thermal Desorption of Surface Hydroxyls on Tin(IV) Oxide

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The structure of the adsorbed layer of water on SnO_2 was investigated by means of thermal desorption, water physisorption, and electron diffraction, using four kinds of SnO_2 samples which differ in method of preparation. Two distinct peaks appear around 513 and 573 K in the thermal-desorption spectra. The peak around 513 K is due to the condensation dehydration of hydroxyls on the (100) plane of SnO_2, on which the two-dimensional condensation of water occurs. The peak around 573 K is associated with that on the (101) plane, on which the physisorption of water is strong and the two-dimensional condensation of water does not occur. The portion of the (100) plane occupied by water molecules is relatively small, and the 1 : 4 ratio (H_2O : OH) holds also on the surfaces on which the two-dimensional condensation of water does not occur. In conclusion, the fully hydroxylated surfaces of SnO_2 are hydrophobic in the sense that they sparsely adsorb water molecules.

In a series of studies[1–4] of the interaction between SnO_2 surfaces and water molecules, we have reported that a two-dimensional condensation of water occurs on the hydrated surface of the SnO_2 obtained from the calcination of stannic acid in air. The electron diffraction of SnO_2 particles and a crystallographic consideration of the hydroxylated surface structure lead to the conclusion that this phenomenon takes place on the surface hydroxyls formed on the (100) plane of SnO_2 with a rutile structure. Furthermore, the ratio of the number of physisorbed water molecules in the monolayer to that of the underlying surface hydroxyls was found to be about 1 : 3—4, indicating a very sparse packing of water molecules in the first physisorbed layer. Since the occurrence of two-dimensional condensation suggests the formation of a close-packed phase of the adsorbate at the monolayer coverage, the fact that water molecules condense two-dimensionally is apparently in conflict with the idea that water molecules are sparsely packed on the same surface.

It may reasonably be expected that there exist crystal planes other than (100), the relative area of which depends on the method of preparation, and that the formation or desorption energy of surface hydroxyls differs on different crystal planes. Therefore, it is interesting to investigate the dependence of the chemisorption or desorption energy of surface hydroxyls upon the nature of the crystal plane. Yamazoe *et al.*[5] reported on the desorbability of chemisorbed water on SnO_2 effected by means of a conventional temperature-programmed desorption technique, as a basis for the development of gas detectors. The aim of the present work is to correlate the peaks in the thermal-desorption spectra of surface hydroxyls to the crystal planes on SnO_2, and also to investigate the above-mentioned contradiction concerning the packing of water molecules on the hydroxylated SnO_2 surfaces.

Experimental

Materials. Tin (IV) oxide of a high purity (99.95%) was obtained from Mitsuwa Pure Chemicals, Ltd.(SnO_2-I). It was prepared by the same method as the sample which we had employed previously,[1–4] *i. e.*, by calcining β-stannic acid formed by oxidizing metallic tin with concd HNO_3. SnO_2-II was obtained by calcining α-stannic acid at 1073 K for 5 h in air, the latter having been prepared by the hydrolysis of $SnCl_4$ with ammonia water.[3] SnO_2-III was prepared by a gas-phase reaction.[6] A mixture of Sn and SnO_2 was heated in a quartz reaction tube at *ca.* 1473 K in a stream of N_2, and the resulting SnO gas was allowed to react with O_2 at the same temperature to give microcrystalline SnO_2 (SnO_2-III). SnO_2-IV was tin (IV) oxide (99.0%) prepared by Wako-Pure Chemicals, Ltd. O_2 and H_2 from a commercial gas cylinder were purified by passing them through a molecular sieve-5A cooled at 195 and 75 K respectively. D_2O (99.75%, Merck) was used without further purification.

Thermal Desorption. As has been described previously,[7] the measurement of the thermal desorption was carried out on a Sartorius vacuum-microbalance. SnO_2 can be readily reduced by evacuation at moderate temperature,[8] and the activity for water adsorption decreased upon reduction.[1,2,4] The surface cleaning of the sample, therefore, was carried out by the following procedure. The sample was evacuated at 773 K for 2 h under a vacuum of 1.3×10^{-2} Pa, heated in O_2 of 13.3 kPa at 773 K for 1 h, cooled room temperature in the O_2 atmosphere, and then evacuated briefly. The reduction of the samples was carried out by exposing the oxygenated sample to H_2 of 6.7 kPa at 433 or 473 K for 2 h. Then, the samples were exposed to saturated water vapor at room temperature for 15 h to ensure a full rehydroxylation of the surface. The thermal-desorption spectra were measured at a heating rate of 5/6 K min^{-1}. The amount of chemisorbed water was determined by the D_2O-exchange method:[9] a fully hydroxylated surface was subjected to three cycles of D_2O vapor exposure (2.0 kPa) at 313 K for 30 min and a subsequent brief evacuation. The number of surface hydroxyls was evaluated from the resulting weight increase in the sample.

Measurement of Water-physisorption Isotherms. The water-physisorption isotherms were measured by using a Sartorius microbalance, except for the case of the measurement of the isosteric heat of physisorption. The sample, rehydrated by the same pretreatment as in the thermal desorption experiments, was evacuated at 313 K for 4 h to remove the physisorbed water, after which the water adsorption was measured at 298 K. The adsorption equilibrium could be usually attained within 10 min, and the resulting isotherm was reversible. The isosteric heat of water physisorption was obtained by applying the Clausius-Clapeyron equation to seven isotherms, which were volumetrically measured in the range from 293 to 308 K. The specific surface area of the samples was determined by applying the BET method to the N_2 adsorption at the temperature of liquid nitrogen.

Residual Gas Analysis during Thermal Desorption. The sample was set into a vacuum line which was essentially identical with that of the thermal-desorption apparatus, and then the temperature was raised at a constant rate of 10/6 K min^{-1} under evacuation. The change in the residual gas pressures was monitored continuously by means of a mass spectrometer, Hitachi RM-50.

Electron-diffraction Analysis. The electron diffraction was used to identify the exposed crystal surfaces of SnO_2. The measurement was made at an accelerating voltage of 200 kV in an electron microscope, Hitachi HU-200E.

Results and Discussion

Thermal-desorption Spectra of Surface Hydroxyls. The thermal-desorption spectra of surface hydroxyls on SnO_2 are shown in Fig. 1, where the desorption rate ($-\mathrm{d}w/\mathrm{d}T$) has been obtained by the graphical differentiation of the original thermal-gravimetrical-analysis curve. Oxygenated samples gave two distinct peaks, around 513 (Peak 1) and 573 K (Peak 2), together with the neighboring shallow peaks, which indicate a complex surface heterogeneity, common to all three samples, SnO_2-I, -II, and -III. Peak 1 is the greatest in SnO_2-I and the smallest in SnO_2-III. On the contrary, Peak 2 is very large in SnO_2-III and smaller in SnO_2-I and -II. These two peaks are united in oxygenated SnO_2-IV, indicating that the desorption energy of surface hydroxyls on this sample is heterogeneous. The H_2 treatment of every sample considerably reduced the height of these peaks or caused the disappearance of the peaks in the thermal-desorption spectra. These results indicate that the H_2 treatment of a sample increases the surface heterogeneity, which is consistent with the results[4)] obtained from the heat of immersion, and that it suppresses the formation of surface hydroxyls.

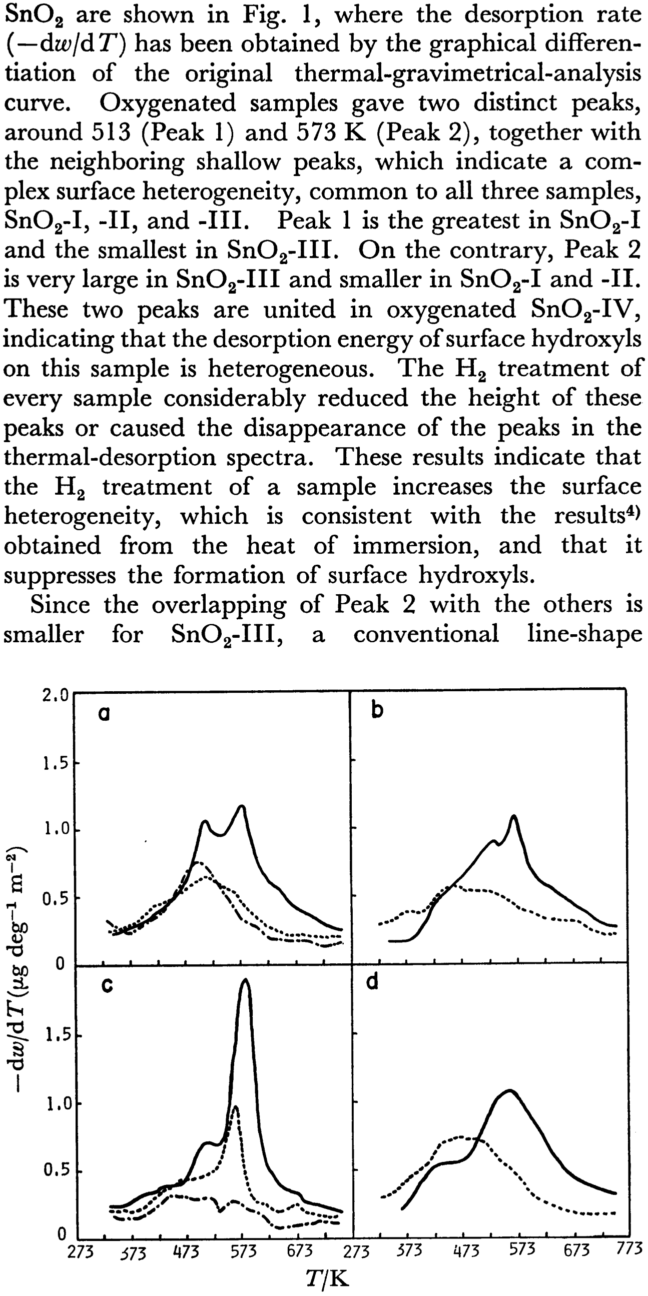

Fig. 1. Thermal desorption spectra of chemisorbed water on SnO_2.
a; SnO_2-I, b; SnO_2-II, c; SnO_2-III, d; SnO_2-IV.
Full line: oxygenated at 773 K, broken line: H_2-reduced at 433 K, dotted broken line: H_2-reduced at 473 K.

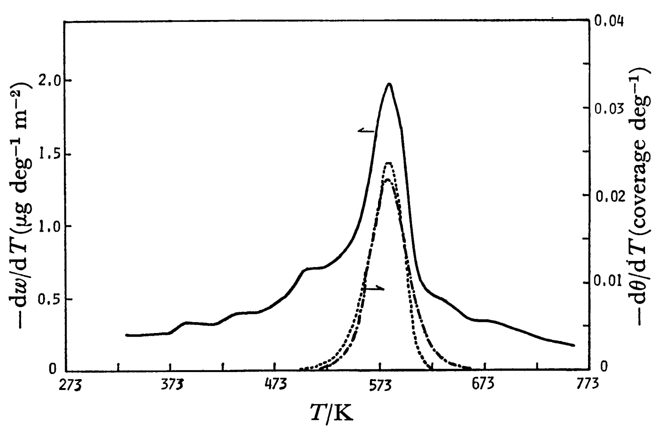

Fig. 2. Line shape analysis of thermal desorption spectrum of chemisorbed water on SnO_2-III.
Full line: experimental, broken line: first order, $E=174$ kJ mol^{-1}, $\nu=3\times10^{12}\ \text{s}^{-1}$, dotted broken line: second order, $E=238$ kJ mol^{-1}, $\nu=3\times10^{18}\ \text{s}^{-1}$.

Since the overlapping of Peak 2 with the others is smaller for SnO_2-III, a conventional line-shape analysis[10)] of this peak allows us to estimate the parameters of the desorption kinetics. In the present study, the activation energy (E) and the frequency factor (ν) of the desorption, which give a peak maximum temperature and a peak half-width similar to those of the observed spectrum, were determined using the Polanyi-Wigner desorption-rate equation:[10)]

$$-\mathrm{d}\theta/\mathrm{d}T=(\nu/\beta)\theta^n\exp(-E/RT) \qquad (1)$$

where β is the heating rate; θ, the surface coverage of the adsorbed species, and n, the order of the desorption reaction. As is shown in Fig. 2, we could obtain the reasonable values of $E=174$ kJ mol^{-1} and $\nu=3\times10^{12}$ s^{-1} with the assumption of a first order or of $E=238$ kJ mol^{-1} and $\nu=3\times10^{18}\ \text{s}^{-1}$ with the assumption of a second order. In any case, it is evident that the surface hydroxyls which gave rise to Peak 2 are uniform in character, in the sense that an observed desorption peak can be approximated by that calculated with a constant value of the desorption-activation energy, E. The maximum temperature of Peak 1 is independent of the preparation method; from its value, the desorption activation energy was calculated to be 153 kJ mol^{-1} at $\nu=3\times10^{12}\ \text{s}^{-1}$ assuming the first-order kinetics.

In the present work, the gravimetric method was adopted for the measurement of the thermal-desorption spectra of surface hydroxyls. Therefore, it is necessary to check whether or not surface species other than the surface hydroxyls are removed, since SnO_2 is readily reduced when it is heated *in vacuo*. The partial pressure of water in the residual gas during thermal-desorption measurements was found to change similarly to the thermal-desorption spectra shown in Fig. 1. The removal of the surface oxygen of SnO_2 by reduction was monitored by measuring the change in the partial pressures of CO, O_2, and CO_2 in the residual gas. The results revealed that the reduction of the sample took place above *ca.* 473 K, and that its influence on the shape of the peaks in the thermal-desorption spectra was insignificant.

Correlation between the Peaks in Thermal-desorption Spectra and the Jump in the Water-adsorption Isotherm. The

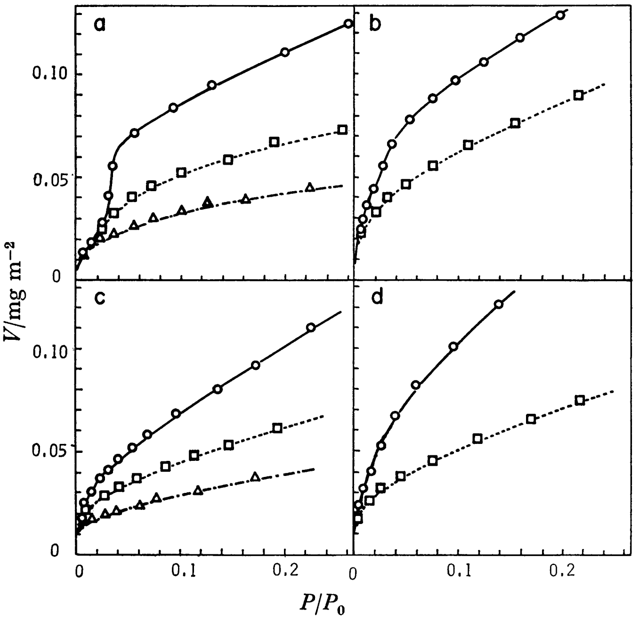

Fig. 3. Adsorption isotherms of water on SnO_2.
a; SnO_2-I, b; SnO_2-II, c; SnO_2-III, d; SnO_2-IV.
(○): Oxygenated at 773 K, (□): H_2-reduced at 433 K, (△): H_2-reduced at 473 K.

water-physisorption isotherms obtained on the oxygenated and reduced samples are illustrated in Fig. 3. It may be seen from Fig. 3 that the shapes of the isotherm vary drastically with the method of preparation and the pretreatment of the sample. The oxygenated SnO_2-I exhibits a clear jump, which arises from the two-dimensional condensation of water,[1] in the range of relative pressures of 0.02—0.04. This jump can be observed slightly on SnO_2-II, but not on SnO_2-III and -IV. The height of Peak 1 in the thermal-desorption spectra decreases in the same order: $SnO_2\text{-I} > SnO_2\text{-II} > SnO_2\text{-III} \simeq SnO_2\text{-IV}$, and becomes negligible in SnO_2-III and IV, as has been stated above. Therefore, it is reasonable to consider that the surface hydroxyls of Peak 1 are closely related to the two-dimensional condensation of water. As was demonstrated in the case of SnO_2-III, the surface hydroxyls of Peak 2 are evidently irrelevant to this phenomenon. H_2-treatment caused a marked decrease in the adsorbed amount and, at the same time, a disappearance of the jump in the isotherms for SnO_2-I and -II.

The relation between the amounts of physisorbed and chemisorbed water on SnO_2 are listed in Table 1. V_p is the monolayer capacity obtained by the B-point method from the adsorption isotherms. V_c is the amount of water chemisorbed expressed by OH groups nm^{-2}, which is obtained from the H-D exchange capacity with D_2O vapor. V_r is the reduced amount of SnO_2 samples, expressed by O atoms nm^{-2}, which was calculated from the weight decrease after H_2 reduction. The last column of Table 1 shows the ratio of the number of physisorbed water molecules in the monolayer to that of the underlying surface hydroxyls. The ratio, which is independent of both the method of preparation and the pretreatment conditions, was found to be about 1:4 (H_2O:OH), as has been reported previously.[1,2] Here, it is interesting to note that H_2-treatment reduces the amounts of both the physisorption and chemisorption of water, and that the ratio remains almost unchanged. This suggests that the ratio of about 1:4 (H_2O:OH) holds on the surfaces which are independent of the occurrence of the jump in the adsorption isotherm.

On the same sample as SnO_2-I which had a clear jump in the isotherm in a previous paper,[2] the isosteric heat (q_{st}-θ) curve exhibited a plateau at the same coverage as the jump appeared, indicating a strong lateral interaction between physisorbed water molecules.[1,2] Fig. 4 shows the q_{st}-θ curves of SnO_2-III and -IV, which have no jump in the adsorption isotherm, together with that of the same sample as SnO_2-I which has been reported in the previous paper.[2] The q_{st} curve of SnO_2-III, whose surface was covered with surface hydroxyls with almost the same desorption energy (Peak 2), has a pronounced plateau in the range of coverage of 0.3—0.7. However, this does not reflect a lateral interaction of physisorbed molecules, which leads to the occurrence of the jump, because no jump appeared in the isotherm. It may be a simple indication of surface homogeneity for water physisorption. As the ratio of V_p to V_c on SnO_2-III as well as

Table 1. RELATION BETWEEN THE AMOUNTS OF PHYSISORBED AND CHEMISORBED WATER ON OXYGENATED AND HYDROGEN-REDUCED SnO_2 SURFACES

	Pretreatment condition	S (m^2/g)	Physisorbed amount V_p (H_2Os/nm^2)	Chemisorbed amount V_c (OHs/nm^2)	Amount of reduction V_r (O atoms/nm^2)	V_p/V_c (H_2O/OH)
SnO_2-I	O_2-773	10.78	2.61	10.40		0.25
	H_2-433		1.61[a]	6.81[a]	1.06[a]	0.24
	H_2-473	10.69	0.97	5.53	3.22	0.18
SnO_2-II	O_2-773	14.17	2.91	10.20		0.29
	H_2-433	12.29	1.81	7.05	1.08	0.26
SnO_2-III	O_2-773	10.87	2.21	10.61		0.21
	H_2-433		1.27[a]	7.23[a]	1.29[a]	0.18
	H_2-473	10.34	0.84	3.03	4.12	0.28
SnO_2-IV	O_2-773	44.44	3.11	12.01		0.26
	H_2-433	45.06	1.44	8.24	0.87	0.17

a) These quantities were evaluated using the surface area of H_2-473.

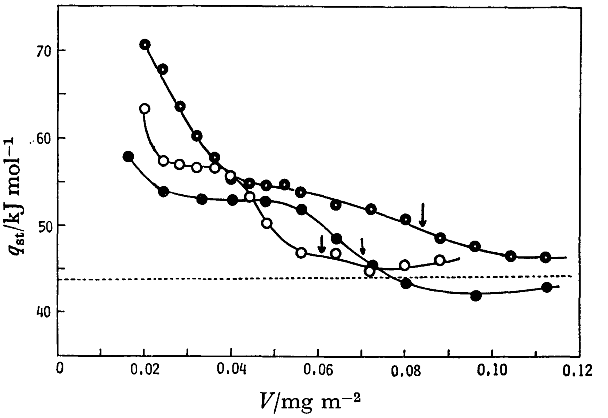

Fig. 4. Isosteric heat of adsorption, q_{st}, of water on SnO_2 as a function of the amount of adsorbed water.
Sample was as follows: SnO_2-III (○); SnO_2-IV (◉); SnO_2-I (●).
A broken line represents the heat of liquefaction of water. Arrows indicate the monolayer coverage of water molecules.

on the other three samples was about 1 : 4, it may be considered that the surface hydroxyls of Peak 2 offer adsorption sites which are homogeneous and separated to such an extent that physisorbed water molecules can not interact with each other. SnO_2-IV, whose surface was covered with surface hydroxyls with a heterogeneous desorption energy, as can be understood from the shallow peak in Fig. 1, gave a q_{st} curve indicating a surface heterogeneity (Fig. 4). The ratio of V_p to V_c on this sample was about 1 : 4, as in the samples with homogeneous surfaces.

The amount of surface hydroxyls giving rise to the two desorption peaks, 1 and 2, in SnO_2-I, which exhibits a clear jump in the physisorption isotherm of water, were estimated roughly from the integrated peak area of the thermal-desorption spectrum. The surface hydroxyls of Peak 1 were only about 7—10% of the total surface hydroxyls, and those of Peak 2, about 13—18%, while the remaining part was occupied by heterogeneous surface hydroxyls. The following conclusion can be drawn from these results: the small ratios of V_p to V_c observed on the SnO_2 sample, where the two-dimensional condensation of water takes place, originated from a simple comparison of the number of the physisorbed water molecules with that of the underlying surface hydroxyls over the whole surface. Thus, it has been found that SnO_2 surfaces, except for the particular ones which are relevant to the two-dimensional condensation of water, are hydrophobic in the sence that they sparsely adsorb water molecules.

Morphological Considerations. Morphological studies[11,12] of the SnO_2 single crystal have shown that the (100), (110), and (101) were well-developed crystal planes, independent of the growing conditions. It was previously inferred[3] from the electron diffraction that SnO_2-I was composed of microcrystals with well-developed (110) and (100) crystal planes. A crystallographic consideration led to the conclusion[2] that the (100) plane of the rutile structure of SnO_2 is responsible for the occurrence of the two-dimensional condensation of water. The electron micrograph of Fig. 5 showed that SnO_2-III was composed of particles with a well-defined shape and with an acute angle; their electron diffraction gave two typical types of diffraction patterns, as is depicted in Fig. 5. The crystallographic analysis proved that these are N patterns of the (101) and (001) planes respectively of the rutile structure of SnO_2. The appearance of the former pattern was more frequent, *i.e.*, more than twice as frequent, than that of the latter. Further, the SnO_2-III sample, which has no jump in the water isotherm, did not give the N pattern of the (100) plane of SnO_2. This provides strong support for the idea that the (100) plane of SnO_2 is responsible for the occurrence of the two-dimensional condensation of water, as was proposed earlier.[2,4]

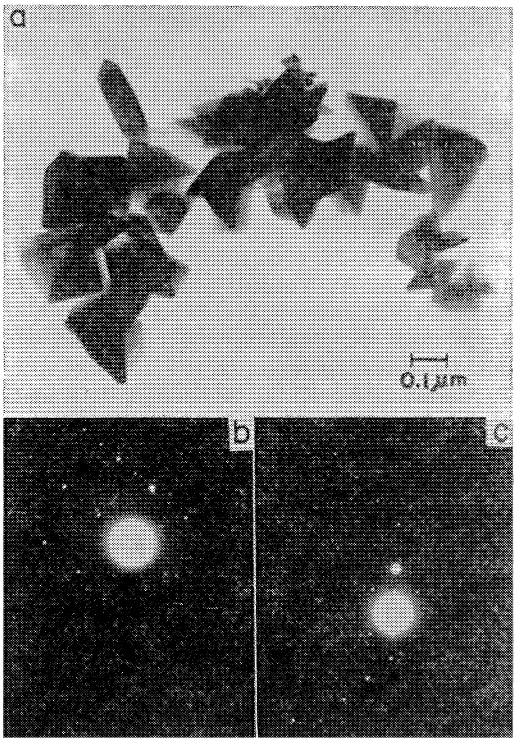

Fig. 5. Electron micrograph (a) and diffraction patterns (b, c) of SnO_2-III. b; N pattern of (101), c; N pattern of (001).

A crystallographic consideration showed that the surface hydroxyls on the (101) plane as well as on the (110) and (111) planes can not form closed hydrogen bonds.[2] Therefore, it may be concluded that the surface hydroxyls on the (101) plane, which give rise to a desorption peak, 2, around 573 K, interact strongly with water molecules through hydrogen bonding, whereas those on the (100) plane, which give rise to a desorption peak, 1, around 513 K, interact with water weakly to cause the two-dimensional condensation on the surfaces. Jones and Hockey[13] suggested that the desorption energy of the surface hydroxyls on the rutile (110) plane changed with the progress of desorption, according to Peri's model,[14] which explains why even uniformly chemisorbed water gives heterogeneous desorption energy on its successive removal. It might be considered that the surface hydroxyls on the (110) plane of SnO_2 desorb *via* a mechanism similar to that on the rutile (110) plane, where a distinct peak can not arise because of its heterogeneous desorption energy.

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