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Relation between Amounts of Chemisorbed Water and Ammonia on Zinc Oxide

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The adsorption isotherm of NH_3 was measured at 25 °C on ZnO surfaces with a controlled amount of surface hydroxyls. It was found that NH_3 can be chemisorbed at 25 °C on the dehydroxylated sites of ZnO in a 1:1 molecular ratio of adsorbed NH_3 to desorbed H_2O. H_2O can be chemisorbed for prechemisorbed NH_3 through exchange reaction to form surface hydroxyls and gaseous NH_3. The physisorption of NH_3 at 25 °C can take place only on a limited part of ZnO surfaces which were fully hydroxylated or ammoniated.

Adsorption studies with the use of NH_3 as a basic adsorbate provide valuable information on the acidic properties of solid surfaces. Many workers have endeavored to investigate the surface properties of silica–alumina and related compounds.[1–6] The principal technique employed was the infrared spectroscopy of NH_3 adsorbed on solid surfaces, giving information on the adsorbed state of the molecules. H_2O molecules are chemisorbed on metal oxides and form surface hydroxyls even at room temperature. They can be desorbed gradually by heating.[7–14] Thus, the surface acidity of a solid is expected to be considerably affected by the existence of surface hydroxyls.[1,15]

The amount of NH_3 adsorbed on hydrated surfaces of MgO or SiO_2 is larger than that on dehydrated ones, since the surface hydroxyls act as the adsorption sites for NH_3.[16,17] Blyholder and Richardson[18] concluded from infrared studies that the sites for chemisorption of NH_3 on α-Fe_2O_3 are the same as those for the chemisorption of H_2O. However, no quantitative relation between the amounts of chemisorbed NH_3 and desorbed hydroxyl has been given.

We have investigated the infrared spectroscopy of NH_3 and H_2O adsorbed on ZnO surfaces with controlled amount of surface hydroxyls.[19] It was found that the adsorbed state of NH_3 depends largely upon the amount of hydroxyls on the surface. We found that the chemisorption of CO_2 occurs on the dehydrated sites of ZnO in such a way that one molecule of CO_2 can be chemisorbed for the removal of two hydroxyls.[20,21] The surface hydroxyls on the fully hydroxylated $(10\bar{1}0)$ planes of ZnO having a wurtzite structure give rise to closed hydrogen bondings with each other, resulting in the appearance of discontinuity in the adsorption isotherm of H_2O because of weakened adsorption force of the surfaces for coming H_2O molecules.[22]

The present work has been undertaken to investigate quantitatively the adsorption of NH_3 on ZnO in connection with the amount of surface hydroxyls, *i.e.*, to investigate the relation between the amounts of chemisorbed NH_3 and dehydroxylated sites on the surfaces of ZnO with controlled amount of surface hydroxyls.

Experimental

Materials. The ZnO sample mainly used was Kadox15 (ZnO–K), prepared by the New Jersey Zinc Co., being the same as that used for infrared studies.[19] Another sample (ZnO–S) prepared by the Sakai Chemical Co. and employed for various examinations,[10,13,22–25] was used for the sake of comparing the data with those of ZnO–K. Both samples gave almost the same adsorption data (Table 1), though their transmittance for infrared beam differs substantially.[19,21]

Measurement of Specific Surface Area. The specific surface area of the samples was measured by the BET method with N_2 adsorption at the temperature of liquid N_2; assumption for the cross-sectional area of a molecule of N_2 was made to be 16.2 Å^2.

Measurement of Adsorption Isotherm. For samples pretreated at 450 °C in a vacuum of 10^{-5} Torr for 4 h, the adsorption isotherms of H_2O and NH_3 were determined volumetrically at 25 °C with a conventional adsorption apparatus equipped with greaseless cocks for NH_3 adsorption and oil-manometer for H_2O adsorption. The pretreatment of the sample at 450 °C *in vacuo* resulted in the removal of almost all the chemisorbed CO_2 and H_2O, leaving only a small amount of chemisorbed H_2O (1.00 OH groups/100 Å^2). The sample was then exposed to saturated H_2O vapor at 25 °C for 12 h, followed by evacuation at 25 °C, which left the fully hydroxylated surfaces with little amount of physisorbed H_2O.[10,13] The last sample was subjected to evacuation at various temperatures from 100 to 400 °C in order to obtain samples of different degrees of hydroxylation, which were used for the measurement of adsorption isotherms of NH_3.

Measurement of Surface H_2O and NH_3 Content. The amount of H_2O or NH_3 chemisorbed was determined by the successive-ignition-loss method.[11] The vapor liberated by heating the NH_3-adsorbed sample was analyzed in the following way. All the vapor evolved in a given temperature range, *e.g.*, 300—400 °C, was condensed in a trap kept in liquid N_2, reevaporated in a closed system at room temperature for measurement of the total pressure, and recondensed in a trap cooled at the dry ice–ethanol temperature at which the pressure of uncondensed gas of NH_3 was measured. After the sample was reevacuated at the dry ice–ethanol temperature, the remaining condensed H_2O, if present, was measured after reevaporation at room temperature. The same procedure was repeated by raising the temperature at appropriate intervals from 25 to 1000 °C. The surface H_2O content, which implies the amount of chemisorbed H_2O remaining on the surface, was calculated by summing the amount of H_2O evolved over the temperature indicated and by assuming that the H_2O content of the sample treated at 1000 °C is nil. The surface NH_3 content was similarly calculated.

Results and Discussion

Adsorption Isotherms of H_2O and NH_3 on ZnO. Figure 1 shows the adsorption isotherms of H_2O and NH_3 on the ZnO–K sample. Curves a and b are the adsorption isotherms of H_2O on the dehydroxylated and fully

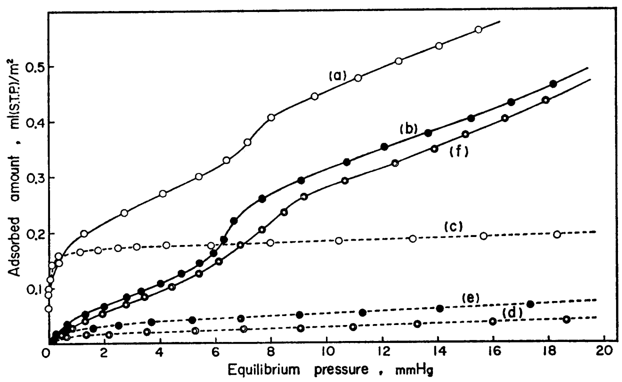

Fig. 1. Adsorption isotherms of H_2O and NH_3 at 25 °C on ZnO surfaces controlled in the amount of chemisorbed H_2O or NH_3. Solid line, H_2O adsorption; broken line, NH_3 adsorption. (a) and (c), on dehydroxylated surface; (b) and (e), on fully hydroxylated surface; (d) and (f), on ammoniated surface.

hydroxylated surfaces, respectively. A large difference is observed between the two curves, because of chemisorption of H_2O on the dehydroxylated surface of ZnO, a distinct discontinuity in the isotherm appearing in the range of relative pressure 0.2—0.3, similar to the case of the ZnO–S sample.[10,13,21–25] Appearance of the discontinuity has been elucidated in terms of the formation of closed hydrogen bonding between the surface hydroxyls on the well-developed (10$\bar{1}$0) planes of the wurtzite structure.[22]

Curve c is the adsorption isotherm of NH_3 at 25 °C on the dehydroxylated surfaces of ZnO–K, curve d being the second adsorption isotherm of NH_3 on the same sample evacuated at 25 °C after the measurement of the first adsorption isotherm. The two curves are of the Langmuir type and seem to be parallel to each other. It seems that the difference of these two isotherms gives the amount of NH_3 chemisorbed on the surface, as in the case of H_2O adsorption. It should be noted that the amount of NH_3 physisorbed at 25 °C on the NH_3-chemisorbed surfaces, which is represented by the second adsorption isotherm, is much smaller than that of H_2O physisorbed at 25 °C, but the amount of chemisorbed NH_3 seems to be as much as that of chemisorbed H_2O. Curve e is the adsorption isotherm of NH_3 at 25 °C on the fully hydroxylated surfaces of ZnO–K. It is seen that the physisorption of NH_3 on the surface hydroxyls is also as small as that on the ammoniated surface (curve d).

The monolayer capacity calculated on these isotherms is given in Table 1, together with the data on ZnO–S. The V_m and V_p values are the monolayer capacity for the first and second adsorption isotherms, calculated by applying the B-point method to the H_2O adsorption isotherms and the Langmuir equation to the NH_3 adsorption isotherms. Since the difference between V_m and V_p gives the chemisorbed amount, we can obtain the chemisorbed amount V_c by subtracting V_p from V_m. As a small amount of chemisorbed H_2O equal to the H_2O content V_h remains on the 450 °C-treated surface, the total amount of chemisorbed H_2O is calculated by summing the values V_c and V_h. The results (Table 1) indicate that the number of NH_3 molecules chemisorbed on dehydroxylated surfaces of ZnO is almost equal to that of chemisorbed H_2O on the same surfaces. This suggests that a molecule of NH_3 is chemisorbed on the sites formed by dehydroxylation of the two neighboring hydroxyls.

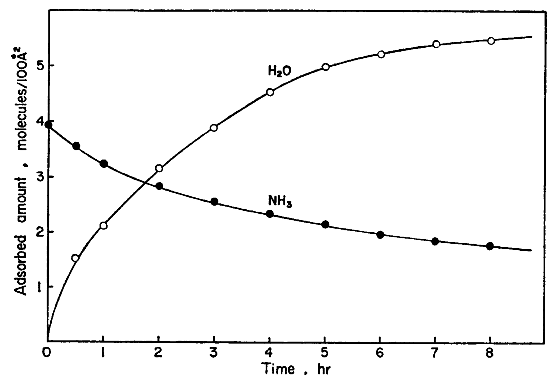

Fig. 2. Exchange reaction of chemisorbed NH_3 on ZnO with H_2O vapor.

Exchange Reaction of Chemisorbed NH_3 on ZnO with H_2O Vapor. Curve f (Fig. 1) is the adsorption isotherm of H_2O at 25 °C on the ammoniated surface of ZnO. The discontinuity in the isotherm reappears in a higher pressure region than in the case of the fully hydroxylated surface of ZnO. Infrared spectroscopic studies have shown qualitatively that NH_3 chemisorbed on ZnO is replaced by H_2O to form hydroxylated surface when exposed to H_2O vapor.[19] Figure 2 shows the change in the amount of chemisorbed H_2O and gaseous NH_3 with time, which was obtained when the ammoniated surface of ZnO was kept in H_2O vapor of the relative pressure 0.7. The equilibrated mixed gas was analyzed by the same procedure as described above. The results (Fig. 2) clearly show that the exchange reaction occurs between the chemisorbed NH_3 and H_2O vapor. The apparently queer phenomenon (curve f, Fig. 1) can thus be interpreted as follows: 1) on account of the exchange reaction the ammoniated surface of ZnO is converted in to the hydroxylated surface, which leads to the appearance of the discontinuity in the adsorption isotherm of H_2O; 2) the shift of the discontinuity to a higher pressure region results from the additional partial pressure of evolved NH_3.

TABLE 1. H_2O AND NH_3 ADSORBED ON ZnO SURFACE

Sample	Surface area (m²/g)	H_2O adsorption V_m, (H₂O molecules/100 Å²)	V_p,	V_c,	V_h,	V_c+V_h, (OH/100Å²)	$\frac{V_p}{V_c+V_h}$, (H₂O/OH)	NH_3 adsorption V_m, (NH₃ molecules/100 Å²)	V_p,	V_c,	$\frac{V_p}{V_c}$,	$\frac{V_c(NH_3)}{V_c(H_2O)}$,
ZnO–K	8.40	11.03	7.50	3.53	0.50	8.06	0.93	5.30	1.35	3.95	0.34	1.05
ZnO–S	3.16	10.63	7.40	3.23	0.65	7.76	0.95	4.69	1.14	3.55	0.32	1.10

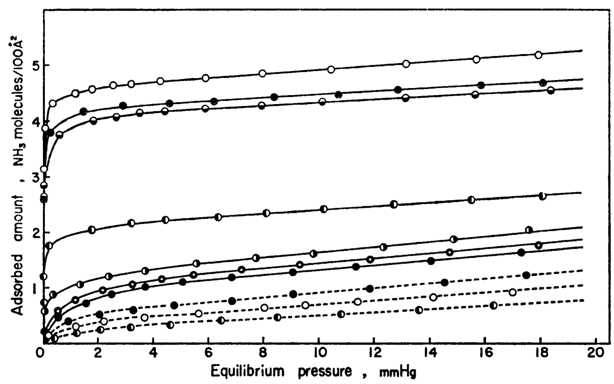

Fig. 3. Adsorption isotherms of NH_3 at 25 °C on differently hydroxylated ZnO prepared by degassing at various temperatures: ●, 25 °C; ◎, 100 °C; ◑, 200 °C; ◐, 300 °C; ◒, 350 °C; ⊙, 400 °C; ○, 450 °C. Solid line, first adsorption; broken line, second adsorption.

Recently, a similar exchange reaction was discovered on a system including H_2O vapor and the ZnO surface covered with chemisorbed CO_2, where CO_2 vapor was liberated from the surface in contact with H_2O vapor.[21)]

Adsorption of NH_3 on ZnO with Controlled Amount of Surface Hydroxyls. The calculations (Table 1) suggest that one molecule of NH_3 can be chemisorbed on the sites formed by the desorption of H_2O. Figure 3 shows the adsorption isotherms of NH_3 at 25 °C on the ZnO samples on which the amount of surface hydroxyls was controlled by degassing the fully hydroxylated surfaces at different temperatures. Solid lines indicate the first adsorption isotherms and broken lines the second ones; some of the latter are omitted but they are all in this narrow range of adsorption amount. The results show that the amount of adsorbed NH_3 increases with increasing temperature of degassing and therefore with decreasing amount of the remaining hydroxyls. We can calculate the monolayer capacity of NH_3, $V_{m(h)}$, by applying the Langmuir equation to the isotherms (Fig. 3), and the amount of chemisorbed NH_3 by substracting the $V_{m(h)}$ value of the second adsorption from that of the first adsorption. The results obtained for the chemisorbed amount of NH_3 are plotted against the degassing temperature (Fig. 4), where the H_2O content of the same sample is also given. We see that the chemisorption of

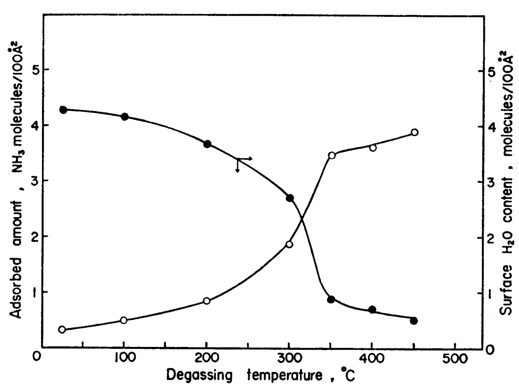

Fig. 4. Dependence of the amount of chemisorbed NH_3 and the surface H_2O content on degassing temperature.

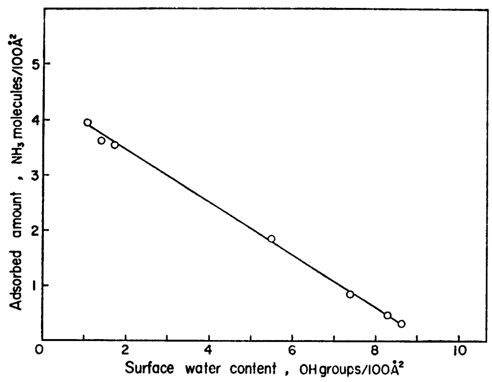

Fig. 5. Relation between the amount of chemisorbed NH_3 and the surface H_2O content.

NH_3 increases with the degassing temperature of the hydroxylated sample, a sharp increase being observed near 300—350 °C which corresponds to a sharp decrease in H_2O content of the sample, and that the sum of the H_2O content and the amount of chemisorbed NH_3 is almost kept constant. This can be seen more clearly from Fig. 5, where the amount of chemisorbed NH_3 is plotted against the remaining surface H_2O content, the linear relationship being observed between the two quantities. This strongly suggests that the chemisorption of NH_3 occurs on the dehydroxylated sites of ZnO in the ratio of one molecule of adsorbed NH_3 to one molecule of desorbed H_2O. A similar relation has been discovered on the chemisorption of CO_2 on ZnO surfaces.[20,21)]

Physisorption of NH_3 on ZnO Surfaces. It might be of interest to infer the nature of a small number of physisorption sites for NH_3 at room temperature. The number of H_2O molecules physisorbed in the first layer on ZnO (Table 1) is identical to that of underlying hydroxyls,[13,22,25)] while the number of physisorbed NH_3 molecules is less than half the number of underlying chemisorbed NH_3. For the surface hydroxyls, the number of physisorbed NH_3 molecules can be calculated from curve e (Fig. 1). This was found to be 1.50 molecules/100 Å², which is approximately the same as 1.35 for the surface with chemisorbed NH_3 (Table 1).

Infrared spectroscopy shows that the adsorption of NH_3 on the fully hydroxylated surface of ZnO takes place through hydrogen bonding and formation of NH_4^+ ions.[19)] The hydroxylated (0001) or (000$\bar{1}$) planes of ZnO will be more active for physisorption of H_2O than the hydroxylated (10$\bar{1}$0) planes,[22)] since they have isolated hydroxyls in contrast to the latter which have closed hydrogen bonding between surface hydroxyls. The former will also be more active for the physisorption of NH_3 than the latter, the sites on the surface defects such as corners, edges and steps being still more active. It seems that the adsorption of NH_3 occurs through hydrogen bonding on the isolated hydroxyls and through formation of NH_4^+ ions on the more active sites as stated above.

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