

Temperature-Programmed Desorption Studies of the Hydrogen-Zinc Oxide System

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Temperature-programmed desorption (TPD) investigations of ZnO (Kadox 25 and oxalate) reveal the existence of six or seven types of surface complexes of hydrogen. They are specified by a temperature range of the maximum rate of desorption. The activation energy of desorption was determined for four types. Three types were assigned by a comparison of TPD results with the published ir and conductivity data.

It was found that the so-called high temperature chemisorption occurs also at low temperatures, even at -35°C .

INTRODUCTION

Adsorption of hydrogen on zinc oxide and the process of its desorption have been studied for many years. Despite this fact even most fundamental questions concerning the system have not been yet answered. A most striking example is the unknown number of surface species. In early works (1, 2) two types were postulated, A and B. Type A was said to be a low temperature chemisorption (say, up to 150°C), and type B, a high temperature one. Eischens *et al.* (3) questioned this view. They claimed, on account of ir data, that at 30°C there may be as many as four different types. The same number of surface species was observed by Narvaez and Taylor (4) although in a rather broad temperature range, from 0 to 400°C . Narayana *et al.* (5, 6) observed two types of chemisorption above 100°C . Scholten and Van Montfoort (7) reported three types at room temperature: (i) reversible and active in ir; (ii) reversible and not active in ir; (iii) irreversible. On the other hand Kokes *et al.* (8-12) claimed the existence of the following types: (i) revers-

ible, occurring rapidly at room temperature, active in ir; (ii) irreversible, occurring at room temperature, ir inactive; (iii) reversible, occurring at -195°C , active in ir; (iv) high temperature chemisorption.

Determination of the number of surface species is complicated by the fact that the so-called "high temperature" chemisorption cannot be excluded at room temperature. We recall an extended polemic on this subject (3, 5, 8).

In 1971 Barański and Cvetanovič (13) investigated the system by the temperature-programmed desorption technique (TPD). They succeeded in observing five surface species denoted as I_A, I_B, II, III, and IV. The B-type, "high temperature" chemisorption, could be identified with TPD peaks III and IV on the basis that they were more significant when adsorbing hydrogen at $200-300^{\circ}\text{C}$. However, no definite conclusion concerning the existence of B-type chemisorption at room temperature could be drawn.

Reversible dissociative chemisorption at room temperature is manifested by two ir

bands, at 3490 and 1705 cm^{-1} (3). According to Eichens *et al.* (3) these are OH and ZnH stretching vibrations, respectively. Using the notation of Dent and Kokes (8) it is a chemisorption of type I. In the previous TPD study it was shown (13) that Dent and Kokes chemisorption I includes species I_A and I_B . Thus peaks I_A and I_B could be related to the ZnH and OH species; a more detailed assignment, however, was not possible there. To solve these problems a new series of TPD experiments has been carried out, the results being compared with those following from the ir method. The significance of such a comparison has already been pointed out (14).

EXPERIMENTAL METHODS

Principles of the TPD method and the apparatus used have been described elsewhere (15, 16). The temperature was increased at a linear rate, β , between 10 and 44°C/min which was kept constant during the whole experiment with an accuracy up to $\pm 2^\circ\text{C}/\text{min}$ for the range -60 to 100°C and up to $\pm 1^\circ\text{C}/\text{min}$ above this range. The highest temperature obtained was 450°C . Commercial 99.8% nitrogen, purified by passage over BTS catalyst (from Badische Anilin and Soda Fabrik), silica gel and through a liquid nitrogen trap, was used as carrier gas at a flow rate of ca. $400 \text{ cm}^3/\text{s}$ at about 30 Torr. The linear velocity of the carrier gas in the vicinity of the sample was about 17 cm/s.

Two different preparations of zinc oxide have been used: ZnO Kadox 25 [obtained by burning of metallic zinc in oxygen (17)] was supplied by New Jersey Co., and belong to the same batch used in previous work (13, 18, 19). ZnO "ex-oxalate" was prepared from solutions of ZnCl_2 with $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The precipitate was dried at 95°C in vacuum, sieved (DIN 0.43 mm) and decomposed in a stream of oxygen for 8 hr at $500 \pm 10^\circ\text{C}$.

Samples used in the experiments consisted of 3-5 pellets (ca. 7 mm ϕ , 5 mm

height) of a total weight 1.2-1.6 g. Each sample was used in experiments consisting of a series of runs. Before the first run the samples were always pretreated with oxygen (100 Torr, 400°C , 1 hr) to oxidize any organic contamination. If not otherwise stated, the samples were always outgassed for 1 hr at 450°C using the vacuum of a diffusion pump. Afterward the samples were brought up to the temperature desired for adsorption. A blank experiment was carried out for all samples before the first run as in Ref. (13).

The surface area of the samples was measured using the BET technique. The measurement was repeated occasionally between two subsequent runs. A tendency to sintering after prolonged use was observed. In an extreme case of a ZnO Kadox

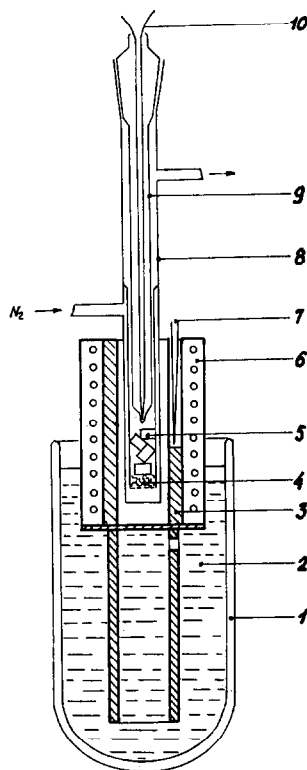


FIG. 1. Experimental arrangement for cooling the sample: (1) Dewar vessel, (2) liquid nitrogen, (3) metallic housing of the heater, (4) glass wool, (5) ZnO pellets, (6) heating spiral, (7) control thermocouple, (8) reactor, (9) pocket of the thermocouple, (10) thermocouple.

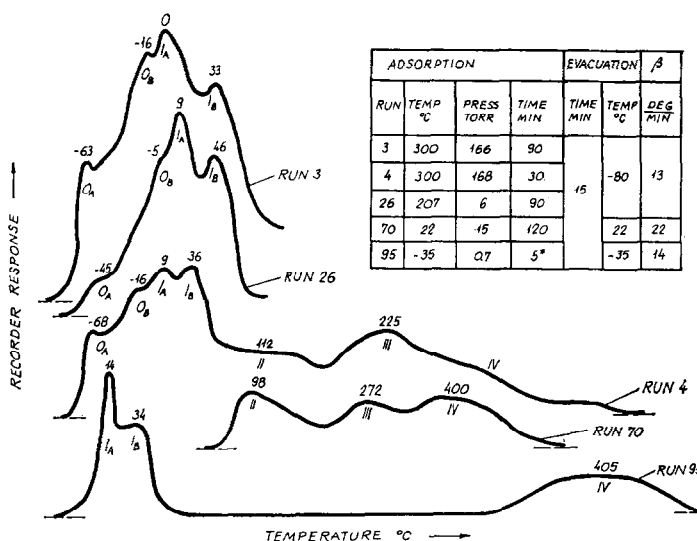


FIG. 2. TPD spectra for desorption of hydrogen from ZnO Kadox. (In Expts 26 and 95 the evacuation was followed by a nitrogen flushing. (*) Time is that at which the initial pressure decreased below 10^{-3} Torr.)

25 sample, the surface area decreased from $8.2 \text{ m}^2/\text{g}$ for a fresh sample to $6.9 \text{ m}^2/\text{g}$ and $4.4 \text{ m}^2/\text{g}$ after 7 and 74 runs, respectively. Owing to these changes in surface area the amounts of hydrogen adsorbed in $\text{cm}^3\text{-}(\text{NTP})/\text{m}^2$ are certainly approximate.

Before storage, commercial 99.8% hydrogen was purified by passage over BTS catalyst, and through a liquid nitrogen trap. The amount of desorbed hydrogen was calculated from the ratio of the area of two peaks, the measured peak and a reference peak obtained by passing a known pulse of hydrogen through the Gow-Mac thermistor thermal conductivity cell used as a TPD detector. A liquid nitrogen trap was always present between the reactor and the detector for the purpose of removing water. Separate experiments proved that no TPD peak originated from adsorption of hydrogen in the empty reactor.

Hydrogen was removed from the gaseous phase before TPD as described earlier (13). However, if removal of the gas at a low temperature was required the reactor was cooled down with liquid nitrogen (see Fig. 1). The temperature given by thermocouple 10 in Fig. 1 varied from -100 to

-130°C . Gaseous hydrogen was then removed by pumping for 15 min or, if its pressure was smaller than 10 Torr, merely by flushing with nitrogen. In the case of pumping, the thermocouple indicated a temporary increase of the temperature up to -90°C (sometimes even -60°C) because of the lack of thermal equilibrium in the reactor. After introduction of the carrier gas the temperature fell to its original value. The liquid nitrogen bath was then removed and when the temperature reached -80°C the furnace was switched on. This moment was taken as the beginning of the TPD run.

TPD spectra were resolved by subtracting well-defined peaks from the experimental curve. The shape of the subtracted peak was assumed to be a regular triangle as a starting approximation and an optimized Gaussian curve in the final approximation.

RESULTS AND DISCUSSION

Number of Surface Species

After adsorption on ZnO Kadox 25 at 300°C and outgassing at -80°C , the TPD spectrum (Fig. 2, run 4) reveals 6 peaks. The seventh one, labeled IV, is hidden in the tail of the preceding peak. However, this peak generally becomes more

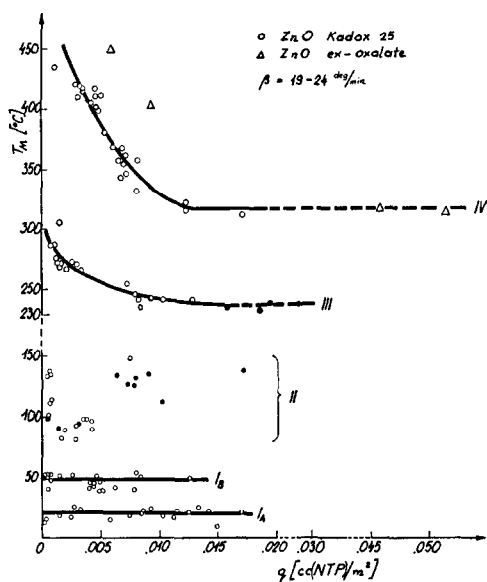


FIG. 3. Dependence of the maximum of the TPD peak (T_M) on the amount of adsorbed hydrogen (q) for species I_A, I_B, II, III, and IV; (●) $\beta = 13$ – $16^\circ\text{C}/\text{min}$.

visible after an adsorption at lower temperatures and pressures (cf. runs 70 and 95 in Fig. 2). Difficulties concerning the separation of peaks III and IV have been discussed elsewhere (18).

The nomenclature of the peaks was adopted from the previous work (13, 18, 19) except for two new peaks, labeled O_A and O_B hereafter.

The TPD spectra for ZnO ex-oxalate and ZnO Kadox 25 are quite similar in spite of the difference in preparation. The only qualitative difference lies in the peak O_A, the existence of which could not be confirmed definitely in the case of the ex-oxalate samples. The total amount of hydrogen adsorbed per square meter is also roughly the same. However, peaks I_A and I_B are enhanced in the case of ZnO Kadox 25 and peaks III and IV in the ex-oxalate oxide.

The similarity of the TPD spectra in the two cases seems to prove that the appearance of the 6–7 peaks is an intrinsic property of solid zinc oxide, and not particularly of ZnO Kadox 25.

A significant overlap of peaks was usually observed. Figure 3 shows the dependence of the temperature of the peak maximum (T_M) on the amount of hydrogen previously adsorbed (q) and refers to experiments where reasonable resolution of the spectrum into peaks was possible. The shape of curves III and IV in Fig. 3 is certainly open to doubt because of the uncertainty of the surface area. No reasonable plot was found for peak II, but the experimental points all lie in the range from 80 to 150°C .

We have found two new surface species of hydrogen, O_A and O_B. In approximately 30 experiments they have been observed as shoulders on the spectrum, in some cases as peaks. The higher the pressure of adsorption and the lower the heating rate, the more significant are these peaks. No significant influence of the time of adsorption was observed for these peaks (see Fig. 2). An accurate calculation of the adsorbed amount of hydrogen of types O_A and O_B was not possible. The difficulty was caused by overlap of these peaks with the I_A peak and by possible losses of the O_A-type species during the evacuation. However, the sum of these two species could be at least estimated. In various experiments it varied from 0.004 to $0.015 \text{ cm}^3(\text{NTP})/\text{m}^2$.

A condition necessary for the appearance of peaks O_A and O_B is a sufficiently low evacuation temperature. This explains why no such peaks were reported in Ref. (13) where the temperature of the bath was taken as the outgassing (here evacuation)

TABLE I
Activation Energies of Desorption

Type of chemisorption	Activation energy for desorption, E_d [kcal/mol]	Coverage interval [$\text{cm}^3(\text{NTP})/\text{m}^2$]
I _A	4.8 ± 0.4	0.007–0.011
I _B	4.4 ± 0.9	0.007–0.013
II	No estimate possible	
III	17.9 ± 3.9	0.010–0.017
IV	20.3 ± 2.2	0.012–0.019

temperature. It is likely that the evacuation of the sample caused an increase of the temperature to such an extent that substantial amounts of species of type O_A and O_B were lost in that previous work.

This lays stress on the importance of an adequate measurement of the evacuation temperature, owing to the disturbance of the thermal equilibrium in the course of evacuation before TPD analysis.

Activation Energies of Desorption

It follows from Fig. 3 that the position of peaks I_A and I_B does not depend on the amount of adsorbed hydrogen. The contrary is true in the case of peaks III and IV. According to Cvetanovič and Amenomiya (15) such a shift is an indication of the heterogeneity of the surface and/or re-adsorption on a homogeneous surface. The lack of shifts of peaks I_A and I_B shows that, in the experimental conditions applied, the re-adsorption of these species does not occur. Therefore it is assumed that no re-adsorption occurs also in the case of species III and IV. It follows that the ZnO surface is homogeneous for I_A and I_B species and simultaneously heterogeneous for species of type III and IV.

The activation energy of desorption, E_a , of a given complex, was determined from experiments in the β range from 10 to 44°C/min and with coverages of the surface which made the position of peaks almost insensitive to changes of the adsorbed amount of hydrogen (cf. Fig. 3). E_a values are given in Table I from which it follows that the activation energies are larger for high temperature peaks III and IV than for the low temperature ones, I_A and I_B . These trends are in general agreement with the results published by Kubokawa (21) apart from a different interpretation.

The E_a values were determined with the aid of Eq. (1)

$$2 \log T_M - \log \beta = \frac{E_a}{2.3RT_M} + \log \frac{E_a}{H}, \quad (1)$$

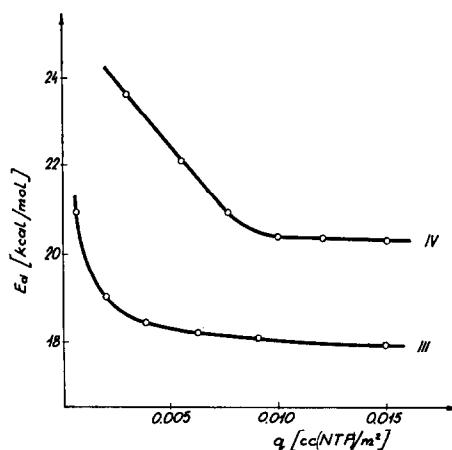


FIG. 4. Dependence of the activation energy of desorption (E_a) on the amount of adsorbed hydrogen (q) for species III and IV.

and a least square fit. Equation (1) fits to several models of desorption although with a different meaning for H (see, for example, the model discussed by Cvetanovič and Amenomiya [Ref. (16), Eq. (11)] or that discussed by Sokolovsky [Ref. (20), Eq. (17)]. The desorption of hydrogen I_A and I_B is considered here with the help of the first of these two models, while the other model is used to describe the desorption of species III and IV.

In order to estimate the dependence of E_a on the coverage for forms III and IV the Cvetanovič and Amenomiya procedure (15) was applied. It was assumed in these calculations that the value of H is independent of the coverage. The E_a values were calculated from Eq. (1) for selected coverages taken from Fig. 3. The results are presented in Fig. 4.

Adsorptions of type I_A , I_B , and IV are fast in contrast to that of type III which is slow (19). From this fact and from the activation energies of desorption a rough estimate of the values of the activation energies of adsorption, E_a , and the heats of adsorption, Q_a , is possible, assuming that the activation energy E_a is the main factor in determining the rate of adsorption and that the process is exothermic ($Q_a > 0$).

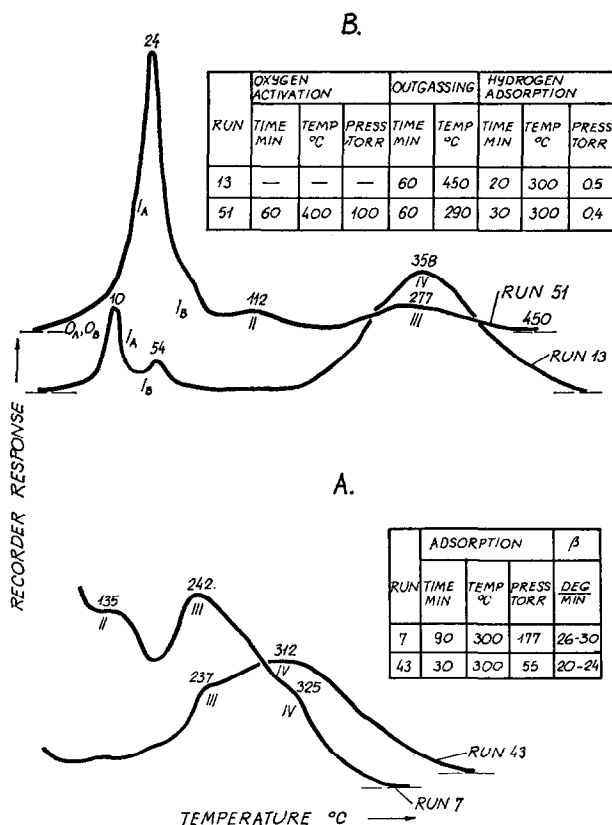


FIG. 5. (A) High temperature part of the TPD spectrum of hydrogen adsorbed on ZnO Kadox 25 (evacuation before TPD at -80°C for 15 min). (B) TPD spectra of hydrogen adsorbed on ZnO Kadox 25 showing the role of activation with oxygen. (In both experiments 15 min nitrogen flushing before TPD; $\beta \approx 22\text{--}24^{\circ}\text{C}/\text{min}$.)

In the case of forms I_A and I_B , $E_d = E_a + Q_a \approx 4$ kcal/mol. Therefore, both E_a and Q_a should be $\lesssim 4$ kcal/mol for these species. For the same reason both $E_a(\text{III})$ and $Q_a(\text{III})$ should be smaller than 18 ± 4 kcal/mol, and $E_d(\text{IV})$, $Q_a(\text{IV})$ smaller than 20 ± 2 kcal/mol. However, adsorption IV is fast in contrast to adsorption III which is slow. Therefore $E_a(\text{IV}) \ll E_a(\text{III})$ and then $Q_a(\text{III}) \ll Q_a(\text{IV})$. One may then conclude that among the forms I_A , I_B , III, and IV the largest heat of adsorption belongs to the form IV.

High Temperature Chemisorption: Effect of Biography

Peaks III and/or IV have been observed in ca. 30 experiments for the adsorption

temperature from -35 to 70°C , at pressures from 0.04 to 250 Torr and adsorption times from 5 to 360 min. The amount of adsorbed hydrogen varied from 0.001 to 0.05 and from 0.001 to $0.03 \text{ cm}^3(\text{NTP})/\text{m}^2$ for peaks IV and III, respectively, depending on experimental conditions.

The reproducibility of TPD results in a given series was good. It enabled us to study the kinetics of the room temperature adsorption of species II, III, and IV (19). However, it was found that the adsorption of hydrogen of high temperature forms, especially of form IV, depends strongly on the biography of the sample. The dependence was investigated for the adsorption temperature of 300°C .

To show the effect let us consider the spectra in Fig. 5A corresponding to runs 7 and 43 of one series. In run 7 the peak IV is marked as a tail only, whereas in run 43 it is rather developed, despite a lower adsorption pressure of hydrogen. Runs 7 and 43 had different adsorption times. However, the adsorption time does not affect the adsorbed amount of hydrogen IV, according to Ref. (19).

However, it was found that the sample was somewhat reduced in the course of the 36 subsequent runs from 7 to 42. The reduction was evidenced by traces of water collected in the cold trap between the reactor and detector. Therefore we thought it worthwhile to study the possible influence of a pretreatment with oxygen, in general and particularly on peak IV.

With this purpose a set of runs was carried out on a sample using an initial pressure of adsorption below 1 Torr. In these experiments, Fig. B5, all the hydrogen of the gaseous phase was rapidly consumed leading to forms I_A, I_B, and IV. Before run 51, the sample had been heated in oxygen and then outgassed at 290°C, a temperature lower than usual. This procedure resulted in a drastic decrease of peak IV. However, after a further outgassing at 450°C, in the subsequent run the peak was visible again, and even more enhanced.

It follows from these experiments that at least the adsorption of type IV is sensitive to the way the sample is prepared and especially to the pretreatment with oxygen.

For more detailed conclusions a further study is required. Promising would be a combined study of two systems: ZnO-H₂ and ZnO-O₂.

Experiment 51 is consistent with Tanaka and Blyholder's TPD results (22) which suggest that preadsorbed oxygen is still present on the zinc oxide surface after the outgassing at 290°C.

Comparison of TPD and ir data

It is interesting to compare TPD data with those obtained by Eischens *et al.* (3) using the ir technique. A set of experiments was carried out at a constant temperature of adsorption, 30°C, and increasing pressures of hydrogen between 0.04 and 160 Torr. After 30 min of adsorption, the system was cooled to -80°C and the gaseous hydrogen was removed. The TPD program was then initiated with a heating rate of $\beta = 10\text{--}13^\circ\text{C}/\text{min}$. Three of the six spectra obtained are reproduced in Fig. 6.

After evacuation at 30°C the small peaks II, III, and IV do not vanish. Therefore they do not represent the reversible, ir active, chemisorption reported for 30°C by Eischens *et al.* (3). Certainly the static experiments of Eischens *et al.* (3) and the present dynamic TPD ones are not completely equivalent. Nevertheless, it is more than probable that the two ir bands are due to the I_A and I_B forms. In TPD experiments these two forms are desorbed at about 20 and 50°C, respectively. The

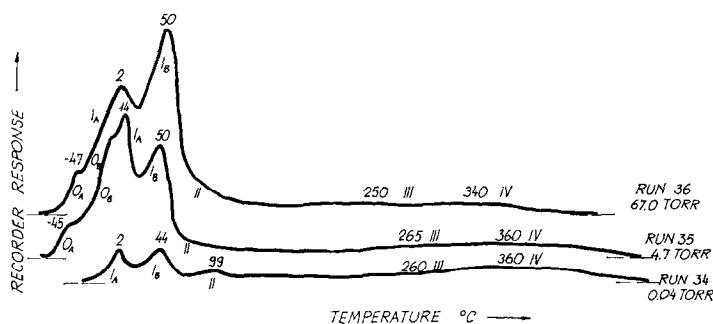


Fig. 6. Selected TPD spectra to be compared with the ir data of Eischens *et al.* (3).

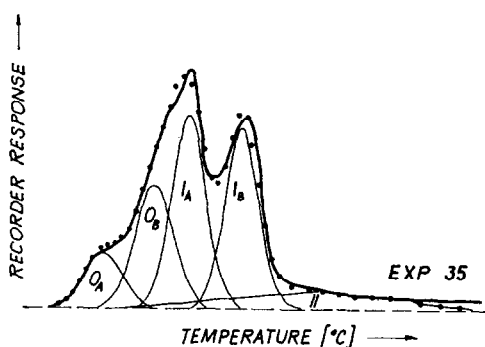


FIG. 7. Example of a resolution of the TPD spectrum by hand; (●) the recalculated values.

forms O_A and O_B can be excluded as their desorption takes place at lower temperatures, from -70 to -50°C and from -20 to -10°C , respectively.

The identification of species I_A and I_B with ZnH and OH is in agreement with the statement of Kokes *et al.* (12) that these two forms cannot be evacuated below -40°C .

A final assignment of forms I_A and I_B follows from a comparative study of the area of TPD peaks and the intensities of appropriate ir bands. In the case of a low pressure (0.04 Torr) both TPD peaks are approximately equal (Fig. 6). A small and not very disturbing peak II is the only other one observed in this TPD spectrum (run 34). The spectra are more complicated in the case of a higher pressure, where

peak II vanishes in the tail of I_B now that the alternative possibility of a large peak II, very close to that of I_B , may be well excluded on account of Fig. 3. On the other hand a significant overlap of peak I_A with peaks O_A and O_B follows from the irregularities on the low temperature side of peak I_A (Fig. 6). Thus it seems safe to conclude that for high pressures peak I_B is larger than peak I_A . This result agrees with the ir intensity measurements of Fischens *et al.* (3) for adsorption pressures higher than 40 Torr (Fig. 8A) where the "excess OH" effect is noticeable. From this fact it follows that peaks I_A and I_B must be ascribed to surface complexes, ZnH and OH, respectively.

With the purpose of a semiquantitative analysis all the six TPD spectra have been resolved by hand (23). A resolution obtained by hand is certainly very approximate and may be disputable. Nevertheless, as shown in Fig. 7, it looks quite reasonable.

Using the calculated amounts of hydrogen adsorbed as form I_A and I_B the Fig. 8B could be drawn. The plots A and B shown in Fig. 8 agree well one with the other in accordance with the suggested assignment of peaks I_A and I_B . On the other hand, if v_{I_A} and v_{I_B} are the amounts of adsorbed hydrogen of type I_A and I_B , respectively, and v_{I_A+B} is the sum $v_{I_A} + v_{I_B}$, these three quantities can be fitted to a Langmuir

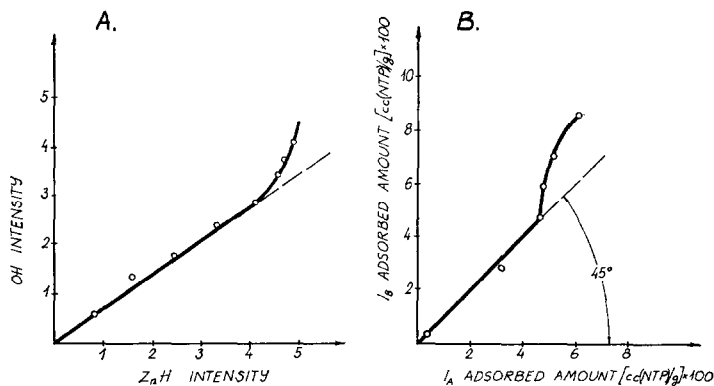


FIG. 8. Comparison of infrared (A) and TPD (B) data. Part A taken from Ref. (3). (B) Ratio of the species I_B and I_A for increasing pressures.

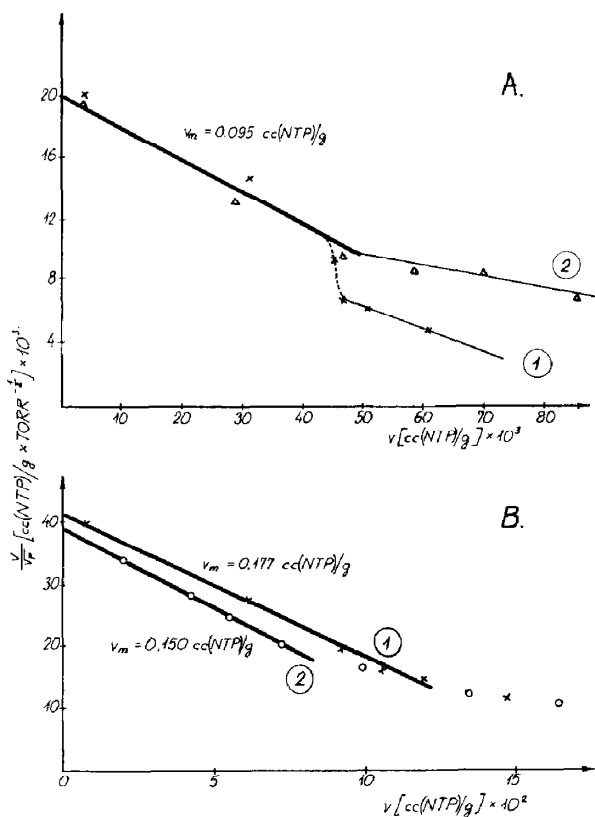


FIG. 9. Langmuir isotherms for dissociative adsorption of H₂. (A1) For the form I_A; (A2) for I_B; (B1) for the sum I_A + I_B; and (B2) for the data taken from Ref. (3).

equation for a dissociative adsorption as shown in Fig. 9. The figure contains also a similar fit of the Eischens *et al.* data taken from Fig. 4 of Ref. (3). From the total amount of chemisorbed hydrogen the value 0.03 cm³/g was subtracted in accordance with that figure (ir inactive adsorption). All plots are linear only for low pressures. The nonlinearity for higher pressures can be caused by "excess hydroxyls." From the slopes of the low pressure parts of all the plots from Fig. 9 the values of a monolayer coverage (v_m) have been calculated. For I_A and I_B they are approximately equal. In the case of $v_{I, A+B}$ the v_m value is of the same order of magnitude as that following from the data of Eischens *et al.* (3). Fitting of the data to the Langmuir equation for a dissociative adsorption supports the assumption of Eischens *et al.* (3) of dissoci-

ative nature of this H₂ adsorption. Using a cross-sectional area for the hydrogen molecule of 0.143 nm², calculated from Eq. 2.64 in the book of Gregg and Sing (24), the saturation chemisorption I_{A+B} is about 10% of the BET argon monolayer. The same order of magnitude was found by Dent and Kokes (5%) (8) and follows also from Eischens and co-workers' (3) results (7%). Thus, ir and TPD data are complementary.

GENERAL DISCUSSION

It might be worthwhile to summarize our results and to compare them with other selected data.

Using the TPD method seven or six hydrogen species have been observed on zinc oxide. Let us discuss the various types of adsorption in the order of decreasing

temperatures of the maxima of desorption peaks.

Forms III and IV

It is now evident that the high temperature chemisorption B consists of two forms, III and IV. This observation is in agreement with the data of Narvaez and Taylor (4) and of Narayana *et al.* (6) and also with results of earlier TPD studies (13). A combined TPD and kinetic study (19) shows that adsorption of type IV is rapid in contrast to that of type III, the latter obeying the Elovich equation. Therefore kinetic studies of the total high temperature chemisorption (1) seem not to be very useful.

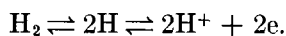
Peak IV has been observed even for adsorptions at -35°C . Peak III has been seen frequently after adsorption at room temperature. In our opinion it gives a final answer to the question of appearance of both these forms at a low temperature. However, another problem arose concerning the significance of the pretreatment (particularly with oxygen).

Adsorption of type III (and II) is slow whereas that of type IV is rapid (19). Type IV adsorption takes place even at pressures lower than 1 Torr (Fig. 2). It is likely therefore that the fast, ir inactive, adsorption found by Eischens *et al.* (3) at 0.1 Torr corresponds to the adsorption of type IV and the slow, inactive one, to adsorption of type II and/or III.

According to Ref. (6) adsorption measurements show a shoulder on the isobar at 180°C . Simultaneously the sample shows a maximum of conductivity at 180°C when heated in gaseous hydrogen from 30 to 300°C . At 30°C the conductivity increases slowly with time in accordance with the Elovich equation. The changes of conductivity are irreversible when the sample is evacuated at 50°C . It follows from these results that the species O_A , O_B , I_A , and I_B (identified by TPD) are not responsible for this effect.

The same seems to be true with complexes of type II because the maxima of their desorption lie at temperatures lower than 180°C (Fig. 3).

The kinetics of the remaining types of adsorption, III and IV, is already known. The adsorption of type III is slow and of the Elovich type. The adsorption of type IV is fast (19). It is concluded, therefore, that the slow increase of conductivity is associated with a formation of surface species of type III. An increase of conductivity is explained by the scheme (6):



Form II

Several authors observed a maximum on the adsorption isobar at about 50°C (1, 4, 6, 26-28). According to most of them the time dependence of the adsorption is that satisfying the Elovich equation. Therefore a slow chemisorption has at least a contribution to this maximum.

The same time dependence was found in our TPD studies of forms II and III. The interpretation of form III was given in the previous section. It follows that form II must contribute to the maximum on the adsorption isobar at 50°C .

There is no maximum observed in the dependence of conductivity on the temperature around 50°C (6). This suggests that in the adsorption of type II no charged species are produced. Adsorption of type II is not typical. It is not described by Eq. (1) and there is no relation between T_M and the amount of adsorbed hydrogen. It is perhaps worthwhile to mention that a very slow adsorption was observed by Dent and Kokes, continuously detectable for several days (8). They interpreted this process as a penetration of hydrogen into the bulk lattice (9). It is possible that peak II is just of this origin.

Forms I_A and I_B

There is a general agreement concerning the chemisorption of type I_A and I_B

(3, 7-13, 29, 30). In the present work it is concluded from the dependence of T_M on the adsorption of hydrogen that the zinc oxide surface is homogeneous for this process. The homogeneity fits well to the Dent and Kokes model (9) based on the stoichiometric structure of ZnO.

It was pointed out by Narvaez and Taylor (4) that "it is not reasonable, though not impossible, that a process adsorbing at higher temperature be paired with a process desorbing at lower temperature since the two types of experiments are not entirely equivalent." Such an expectation was fulfilled in the present study. The chemisorption observed by Narayana *et al.* (5, 6) around 180°C could be paired with species of type III noticed by the TPD peak at 240-300°C. Likewise, form II has at least a contribution to the adsorption isobar at about 50°C. The corresponding TPD peak was found in the interval from 60-100°C in a previous work (13) and in the interval from 80-150°C in the present one. According to these observations, the TPD peaks I_A and I_B lying in the range from 0 to 50°C should give a maximum in the isobar below 0°C. Unfortunately no such a maximum has been reported so far. Clearly this point requires a further study.

Eischens *et al.* (3) claimed that hydroxyls in excess form a different type of chemisorption. Our TPD results, however, do not reveal any differentiation of I_B species.

The excess of hydroxyl groups at high pressures could be explained if the model of Dent and Kokes (9) is recognized.

It has been shown that peak I_A has its origin in ZnH. According to a previous work (13) the I_A species are mainly consumed when hydrogenating ethylene. It follows that the ZnH species play an active role in the reaction of $C_2H_4 + H_2 = C_2H_6$ catalyzed by ZnO.

Forms O_A and O_B

This is a first announcement of the TPD peaks O_A and O_B and the results should be

considered as preliminary. Chemisorption within the temperature range from -195 to 0°C was observed by several authors using other techniques (2, 5, 10, 31). Chang *et al.* (10, 11) deduced from ir data that molecular hydrogen is adsorbed at these temperatures. According to Narayana *et al.* (5) the conductivity changes at -78°C are reversible and depend on the pressure of hydrogen. However, a more systematic study is desirable to link these results.

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REFERENCES

1. Taylor, H. S., and Strother, C. O., *J. Amer. Chem. Soc.* **56**, 586 (1934).
2. Kesavulu, V., and Taylor, H. A., *J. Phys. Chem.* **64**, 1124 (1960).
3. Eischens, R. P., Pliskin, W. A., and Low, M. J. D., *J. Catal.* **1**, 180 (1962).
4. Narvaez, R., and Taylor, H. A., *J. Phys. Chem.* **69**, 2500 (1965).
5. Narayana, D., Lal, J., and Kesavulu, V., *J. Phys. Chem.* **74**, 4150 (1970).
6. Narayana, D., Subrahmanyam, V. S., Lal, J., Mahmood Ali, M., and Kesavulu, V., *J. Phys. Chem.* **74**, 779 (1970).
7. Scholten, J. J. F., and Van Montfoort, A., in "Proceedings of the Fifth International Congress of Catalysis, 1972" (J. W. Hightower, Ed.), Vol. 1, p. 385. North-Holland, Amsterdam.
8. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **73**, 3772 (1969).
9. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **73**, 3781 (1969).
10. Chang, C. C., and Kokes, R. J., *J. Amer. Chem. Soc.* **93**, 7107 (1971).
11. Chang, C. C., Dixon, L. T., and Kokes, R. J., *J. Phys. Chem.* **77**, 2635 (1973).
12. Kokes, R. J., Dent, A. L., Chang, C. C., and Dixon, L. T., *J. Amer. Chem. Soc.* **94**, 4429 (1972).
13. Barański, A., and Cvetanović, R. J., *J. Phys. Chem.* **75**, 208 (1971).
14. Amenomiya, Y., *Shokubai* **11**, 88 (1969).
15. Cvetanović, R. J., and Amenomiya, Y., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 17, pp. 103, Academic Press, New York, 1967.

16. Cvetanovič, R. J., and Amenomiya, Y., *Catal. Rev.* **6**, 21 (1972).
17. According to the New Jersey Zinc Co., ZnO Kadox 25 is manufactured by the so-called French process mentioned in Brown, H. E., "Zinc Oxide Rediscovered," p. 12, New Jersey Zinc Co., New York, 1957.
18. Barański, A., Cvetanovič, R. J., Dal, T., and Gałuszka, J., Proc. II Int. Symp. Heterog. Catalysis, Varna, November, 1971, published in Comm. of the Dept. of Chemistry, Bulgarian Academy of Sciences, **6**, 135 (1973).
19. Barański, A., Diakovitch, V., and Gałuszka, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **21**, 611 (1973). (Kinetic studies in experiments no. 60-70 were carried out using the same Kadox 25 sample as in the present work.)
20. Sokolovski, V. D., *Kinet. Katal.* **11**, 1492 (1970).
21. Kubokawa, Y., *Bull. Chem. Soc. Japan* **33**, 546, 936 (1960).
22. Tanaka, K., and Blyholder, G., *J. Phys. Chem.* **76**, 3184 (1972).
23. Kaiser, R., and Klier, M., *Chromatographia* **2**, 559 (1969).
24. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity," p. 67, Academic Press, New York, 1967.
25. Green, M., "Solid State Surface Science," p. 31. Russian ed., Mir, Moscow, 1972.
26. Cimino, A., Molinari, E., and Cipollini, E., *Actes Congr. Int. Catal. 2nd, 1960*, p. 263 (1961).
27. Cimino, A., Cipollini, E., Molinari, E., Liuti, G., and Manes, L., *Gazz. Chim. Ital.* **90**, 91 (1960).
28. Low, M. J. D., *Canad. J. Chem.* **37**, 1916 (1959).
29. Naito, S., Shimizu, H., Hagiwara, E., Onishi, T., and Tamaru, K., *Trans. Faraday Soc.* **67**, 1519 (1971).
30. Naito, S., Shimizu, H., Hagiwara, E., Onishi, T., and Tamaru, K., *Bull. Chem. Soc. Japan* **43**, 974 (1970).
31. Taylor, H. S., and Liang, S. C., *J. Amer. Chem. Soc.* **69**, 1306 (1947).