

Pressure Effects on Hydrogen Chemisorption on Zinc Oxide

Manfred J. D. Low

Contribution from the School of Chemistry, Rutgers, The State University,
New Brunswick, New Jersey. Received April 11, 1964

Experiments on the effects of pressure on the chemisorption of hydrogen on zinc oxide were made. The various data suggest that weakly bonded ZnH and OH surface species (type W) are precursors to more tightly bonded species (type P). Two distinct pressure effects exist, the ambient pressure controlling the concentration of type W until a "saturation" of the surface is reached and the initial pressure controlling the degree of saturation that may be achieved. The rate of conversion of type W to type P is rate controlling in chemisorption kinetics.

Introduction

The chemisorption of hydrogen on zinc oxide has received much attention during the past 30 years, and a voluminous literature on that topic has developed. Some of the mechanisms postulated to explain the various effects found were reviewed recently by Eischens, Pliskin, and Low,¹ who also described the results of a series of experiments on the infrared spectra produced when hydrogen was chemisorbed on zinc oxide. That study showed that hydrogen chemisorbed on pure zinc oxide at temperatures between 30 and 130° produced infrared absorption bands at 2.86 and 5.85 μ attributable to oxygen-hydrogen and zinc-hydrogen stretching vibrations. The hydrogen of these covalent OH and ZnH surface species was weakly bound, the adsorption being easily reversible and pressure sensitive. In addition to the weakly bound species, there was a slow, more tightly bound chemisorption that did not produce detectable infrared bands, the hydrogen being considered to be adsorbed in a protonic form. The ratio of the intensities of the OH and ZnH infrared bands remained constant as the intensities of both bands increased linearly with increasing hydrogen pressure up to about 4 cm. Above a pressure of 4 cm., an excess of loosely bonded OH with respect to ZnH was observed. On the basis of this linearity, it was concluded that there was a constant ratio in the number of OH and ZnH groups found, a reasonable assumption being that the ratio was unity and that the weakly bonded chemisorption process observed resulted from a splitting of hydrogen molecules by zinc-oxygen pairs on the surface to form OH and ZnH structures. There was, however, little information on pressure effects on the chemisorption of hydrogen on zinc oxide. That deficiency suggested the present study. Also a review² of pressure effects implied that these were far from clear and also suggested work on this topic.

Experimental

An adsorption system³ of the type used by Taylor and Strother⁴ was modified by the addition of calibrated

(1) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catalysis*, **1**, 180 (1962).

(2) M. J. D. Low, *Chem. Rev.*, **60**, 281 (1960).

(3) M. J. D. Low, *Can. J. Chem.*, **37**, 1916 (1959).

Toepler bulbs so that the volume of the system could be rapidly expanded or contracted at will. The system was suitable for "constant volume" (CV) rate experiments, during the course of which the ambient pressure, P_a , within the system fell continuously, as well as for "constant pressure" (CP) rate experiments, the volume of the system being then decreased by addition of mercury in amounts equal to the volume of gas taken up. The initial pressure, P_s , is that pressure calculated to exist after the introduction of the adsorbate assuming that adsorption does not occur; $P_s = P_a$ in a CP system.

Tank hydrogen was purified by diffusion through hot palladium. All experiments were carried out at a constant temperature of 80° in the region of the low-temperature chemisorption maximum.³ Other experimental details are described elsewhere.³ Two adsorbents of zinc oxide (from the oxalate)³ having a surface area of 16 m.²/g. were used. Adsorbent A, used with experiments of set A, was 25 g. of powder. Adsorbent B, used for the pressure variation experiments of set B, was 20 g. of powder pressed at 1 ton/in.² into pellets without binder. Similar adsorption effects were observed with powder and pellet samples, but the latter were used to prevent loss of adsorbent during rapid changes in pressure.

Experiments, Results, and Discussion

Kinetics of Chemisorption. For the kinetic experiments done under CV or CP conditions, if the amount of hydrogen q , adsorbed at time t , is plotted vs. the logarithm of t , plots such as those of Figure 1 result. Many plots consist of two linear portions, the point of intersection varying from about 16 to 19 ml. It has been shown elsewhere³ that these "breaks" are not kinetic artifacts and are to be found quite frequently.² The plots of most data obtained at pressures below about 30 cm. are linear throughout. The experiments resulting in such unbroken plots were stopped before q had reached the region in which a change in slope appears in plots of experiments at higher pressures.

The linear sections of plots of data of CV as well as CP experiments can be described by an integrated form of the Elovich equation^{2,5}

$$q = (2.3/\alpha) \log(a\alpha t)$$

Such prescription is precise, despite the relatively large pressure diminutions occurring during the course of CV experiments. The various effects described below are, obviously, independent of the formulation of the kinetics. The Elovich equation is used for clarity and precision of representation of the data.

Some typical data on pressure drops are shown in Table I.

(4) H. S. Taylor and C. O. Strother, *J. Am. Chem. Soc.*, **56**, 586 (1934).

(5) H. A. Taylor and N. Thon, *ibid.*, **74**, 4169 (1952).

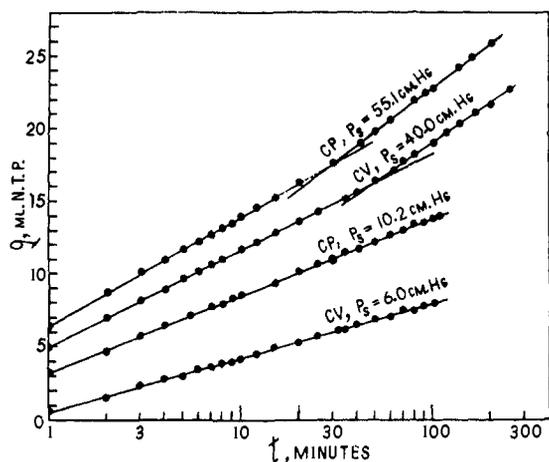


Figure 1. Kinetics of chemisorption: data of set A, 80°, examples of CV and CP experiments.

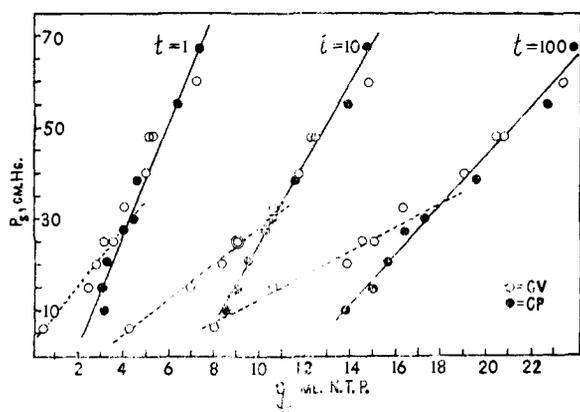


Figure 2. Volumes adsorbed after various times: data of set A, 80°; comparison of CV and CP experiments.

Comparison of CV and CP Experiments. The CV-CP data of set A are summarized by the plots of Figures 2 and 3. Amounts of hydrogen taken up after 1, 10, and 100 min. for various P_s values are shown in Figure 2. Above about 30 cm., the data points of Figure 2 fall about the same solid lines. Below that pressure, however, the CV points deviate considerably from the solid lines going through all of the CP points and also through the CV points at higher pressures. This deviation is indicated by the dashed lines, showing that uptake under CV conditions is less voluminous and slower than under CP conditions at pressures below about 30 cm.

Table I. Pressure Diminution during Some CV Runs^a

P_s $t = 0$	$-100(P_s - P_t)/P_s$ $t = 1$	$t = 100$
48.0	6	24
25.0	13	41
15.0	20	58
9.9	35	88

^a P_s and P_t in cm.; t in min.

A similar trend is reflected by the plots of Figure 3. The slope of the q - $\log t$ plots is $2.3/\alpha$. Also, the rate at any time t equals $2.3/\alpha t$, so that a comparison of re-

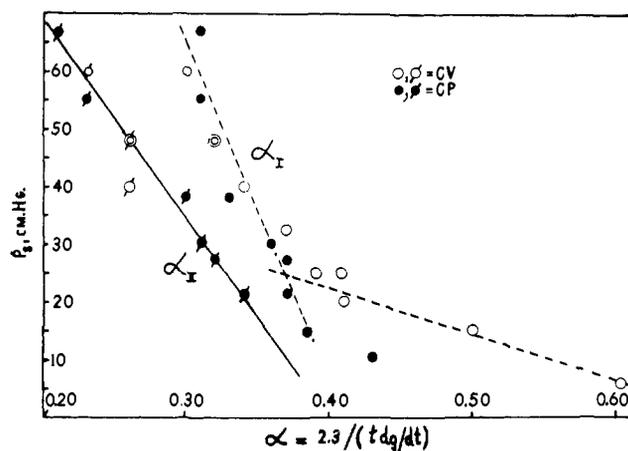


Figure 3. Kinetics under CP and CV conditions: data of set A, 80°; comparison of α values.

ciprocal α -values is equivalent to a comparison of rates at identical times. The plots marked α_1 and α_{11} of Figure 3 refer to the first and second linear segments of q - $\log t$ plots such as are shown in Figure 1. For some low pressure runs, where the q - $\log t$ plots are linear throughout, α_{11} values are not available. At P_s values higher than about 30 cm., the rates of CV and CP experiments are seen to be comparable, as shown by the scatter of CV and CP values for α_1 or for α_{11} about the same line. Below pressures of about 30 cm., however, there is a marked deviation of α_1 values from the trend shown at higher P_s ; or, at low pressures, the rates of adsorption under CV conditions are somewhat slower, and amounts adsorbed are less voluminous than are those measured under CP conditions.

The usual application of the Elovich equation to the value of αa at a given time yields α -values only if the value of a is constant. There is an alternative, namely, that α is constant and the value of a is changing. Thus, the apparent increase in α -values shown in Figure 3 may simply reflect a real decrease in the value of a , and the linearity with pressure, a not unlikely first-order dependence on P_a .

The differences between CP and CV experiments appear to be connected with the relatively large pressure drops observed during CV experiments at low P_s values. At $P_s = 30$ cm., the pressure drop after 1 min. begins to exceed 10%, and at lower P_s is seen to be quite severe, as shown in Table I. At higher P_s the data are not sensitive enough to discriminate effects ascribable to small pressure diminutions.

In view of the spectroscopic data, the measured amount of hydrogen adsorbed must be taken as the sum of the amounts of weakly and strongly bound species. A rate of gas uptake thus measures the overall effect and, by itself, is not very meaningful if the contributions due to the various species cannot be distinguished.

Pressure Fluctuations. Adsorbent A was used in some experiments under CV conditions during which abrupt pressure fluctuations were induced by opening the system to an evacuated Toepler bulb of known volume. After a certain time the gas was forced out of the bulb, and the system was restored to "normal" conditions. Figure 4 shows the effect of such a series

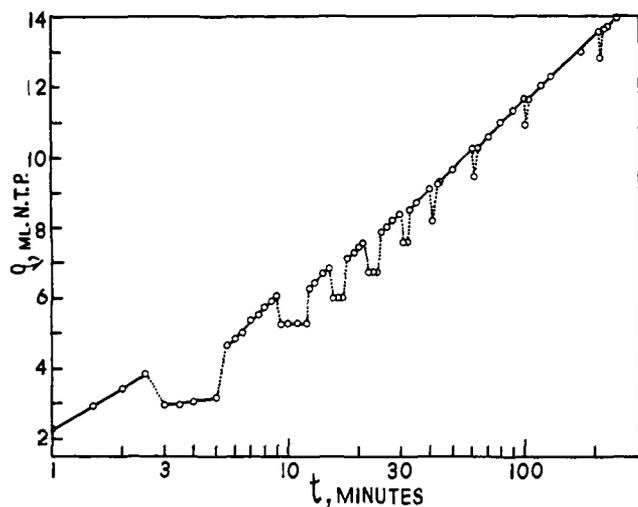


Figure 4. The effects of pressure fluctuations: data of set A, 80°; the volume of the adsorption system was rapidly increased, kept constant for a time, and then was rapidly decreased to the original volume.

of pressure fluctuations. At $t = 2.5$ min., for example, the pressure was abruptly dropped from 37.90 to 14.50 cm., and then was abruptly raised from 14.37 to 37.38 cm. at $t = 5$ min. Rapid desorption of 0.88 ml. and adsorption of 1.50 ml. of hydrogen, respectively, accompanied the pressure drop and rise. In each case of a pressure fluctuation there was a rapid ad- or desorption. The amount rapidly desorbed was smaller than the subsequent amount rapidly adsorbed, but the general trend is for the desorption to increase and the adsorption to decrease until, at about 50 min., their magnitudes are roughly equal.

It is interesting to note that the amounts of gas ad- or desorbed are time dependent, changing in magnitude with increasing time. A similar trend is shown by the plots of Figure 1, where the ratios of amounts taken up under CP and CV conditions below about 30 cm. tend to decrease with time. At the lowest pressure of 6 cm., for example, the estimated amount taken up under CV conditions changes from about 20% of that estimated to be taken up under CP conditions at $t = 1$ min. to about 50% at $t = 10$ min., and is about 60% at $t = 100$ min.

A similar time dependence is described by Kubokawa,⁶ who exposed zinc oxide to hydrogen for 15 min. in one experiment and for 16 hr. in another. A known amount of gas was pumped out of the system after each exposure, and the rate of desorption was then measured. The desorption rates corresponding to equal amounts adsorbed differed markedly with time of exposure.

The infrared work had shown the existence of weakly bound OH and ZnH surface species, hereafter termed type W. The adsorption producing those species was easily reversible and pressure sensitive. On the basis of those results it seems not implausible to ascribe the present instantaneous gas uptakes and evolutions to the formation and destruction of the type W species. If such an identity of adsorptions is assumed, and it seems reasonable to do so, then the effects suggest that there is a conversion of one type of adsorption

(6) Y. Kubokawa, *Bull. Chem. Soc. Japan*, 33, 550 (1960).

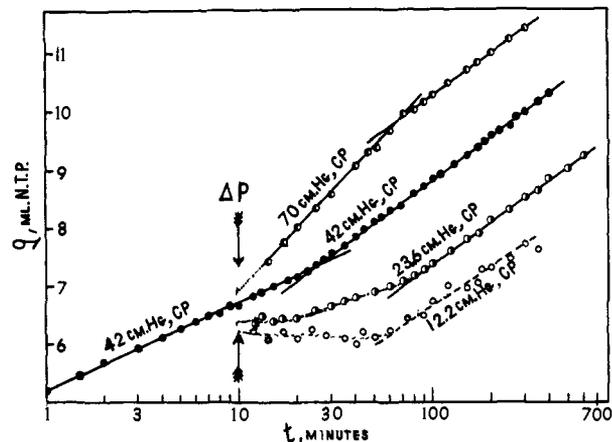


Figure 5. The effects of abrupt pressure changes: data of set B, 80°; at ΔP , the pressure was abruptly changed to a new, constant value.

to another, e.g., type W converting to the protonic or similar form, hereafter termed type P; or that a rearrangement of the distribution of adatoms occurs, i.e., there is surface migration; or both effects occur.

Abrupt Pressure Changes from Constant Pressure. In order to define pressure effects further, abrupt pressure changes were made during adsorption experiments proceeding under CP conditions. Thus, a run was started at a certain initial pressure P_s , which was kept constant until a predetermined time t . At t the pressure within the system was abruptly changed to a new and subsequently constant pressure P_2 . One series, termed B, of such experiments was made with adsorbent B. For purposes of comparison, several runs were made under "normal" conditions, i.e., unperturbed by abrupt pressure changes. Such data are summarized in Table II.

Table II. Abrupt Changes from Constant Pressure

Run no.	P_s , cm.	P_2 , cm.	t , min.	α_1	α_2	α_{int}	α_{final}
1	42.05	1.62	0.94
2	42.08	1.58	0.94
3	42.02	23.61	10	1.64	...	Curved	0.95
4	42.10	70.10	10	1.62	...	0.67	0.95
5	42.05	12.2	10	1.60	...	Curved	0.94
6	70.35	1.28	0.82
7	70.22	42.07	22	1.28	...	1.50	0.82
8	70.50	42.05	22	1.28	...	1.58	0.88
9	70.40	1.28	0.82

The plots of Figure 5 illustrate such experiments. The plot of solid circles represents duplicate and undisturbed runs at $P_s = P_a = 42$ cm. under CP conditions. Further runs under identical conditions were then made, repeating also the range from 1 to 10 min. The data points in that period are not shown (to avoid crowding the plot) and replicate the "normal" runs over that period. At $t = 10$ min., however, the system pressure was abruptly raised, or lowered, this point being indicated by the arrows at ΔP on Figure 5. The data obtained after the pressure had been abruptly changed to a new and subsequently constant value are shown by the plots with open or partially filled circles.

Several minutes were required to readjust the atomic CP device, so that measurements immediately following a pressure change are not available, but extrapolation of subsequent data to the time of pressure change shows that instantaneous ad- and desorptions of gas occurred.

Following the pressure change from 42 to 70.1 cm., the adsorption was faster than encountered in an unperturbed experiment done at 70 cm. When the pressure was dropped to 23.6 cm., no change in adsorption was observed for some 10 min. Similarly, when the pressure was dropped to 12.2 cm., no change was detected for about 50 min. These "intermediate" regions were followed, in each case, by a region in which the value of α was the same as that of unperturbed experiments at 42 cm.

The instantaneous ad- and desorptions are again attributed to type W species, as in pressure-fluctuation experiments. The "intermediate" regions again point to a conversion of one type of adsorbed species to another and/or to a surface diffusion effect. Similar intermediate regions occur with the pressure fluctuations, as in Figure 4, ascribable to the same effects. The regions of slower rate would not be expected to be caused solely by a slow desorption of the type W species because Taylor and Kesavulu⁷ state that the activation energy for this adsorption is zero so that the desorption could be expected to be rapid, but could be caused by (a) the direct desorption of type P, or by (b) the conversion of type P to type W followed by instantaneous desorption of the latter, or (c) a surface diffusion-controlled desorption involving type W.

There is an apparent inconsistency between the P_a dependence shown by the kinetic experiments of set A and the P_a independence of the experiments during which there were abrupt changes in P_a . This cannot be resolved by a simple statement that above a certain pressure (in this case, about 30 cm.) the system is relatively insensitive to pressure, because P_a was dropped to values lying within the pressure-sensitive range after 10 min., and there were no significant differences in adsorption rates after the "intermediate" regions. This suggests, rather, that two types of pressure effects are operative, and that one or the other predominates, depending on the degree of surface coverage.

The rate of conversion of type W to type P may be the rate-controlling step in the adsorption. Some evidence for this comes from the infrared work, which showed that as P_a was increased over 4 cm., there were no further increases in intensities of the infrared absorption bands attributed to the type W species, although slow adsorption continued; the surface was "saturated" with type W, and a further increase in P_a could not increase the surface concentration of those species. This

(7) V. Kesavulu and H. A. Taylor, *J. Phys. Chem.*, **63**, 1317 (1959); **66**, 54 (1962).

suggests that the rate of passage of electrons over some potential barrier, or similar mechanism, is involved in type P adsorption. In this case, one would expect the rates of chemisorption of the hydrogen isotopes to be identical, as suggested by Kesavulu and Taylor,⁷ because the rate-controlling step is an electronic one. The surface concentration of type W species, and also hence the over-all adsorption, appears to be a function of P_a until "saturation" is reached. The point of saturation, however, seems to be independent of P_a and to be a function of P_s . This is shown by the kinetic data of set A and the pressure-change experiments of set B. On producing abrupt changes in P_a , a disturbance of the surface occurred but, after the "intermediate" regions, there were no significant differences in adsorption rate. This suggests that, both before and after a pressure change had occurred, a saturation of the surface with type W had occurred so that effects of P_a were minimized. The saturation, however, occurred at pressures below the apparent "saturation pressure" of about 30 cm. indicated by the data of set A; or, the degree of saturation, e.g., the surface concentration of Zn atoms, appears to be a function of P_s rather than P_a . Such a "memory effect" of initial conditions by the surface requires a mechanism involving some site-creation process, and formal mechanisms capable of accounting for such effects have been described and are reviewed elsewhere.² Parenthetically, if the Elovich equation is considered to apply, then the various effects can be considered to be evidence for a mechanism of chemisorption which has been suggested for those processes accountable by the Elovich equation, namely, the surface migration of atoms from a weakly to a more strongly chemisorbed state.⁸

It is possible that the P_s dependence may be connected with heating effects produced when the clean surface is first exposed to an adsorbable gas.⁹ A rapid exothermic reaction may be expected to occur under pseudo-adiabatic conditions, which would result in intense local heating of the surface. The rapid heating and subsequent quenching could condition the surface to an extent proportional to P_s , i.e., induce strains or modifications of surface structure, or remove impurities, or, with ZnO, bring about a change in the composition of the surface by causing desorption of oxygen so that abnormal stoichiometric conditions result.

Acknowledgment. Support by grants from Division of Air Pollution, Bureau of State Services, Public Health Services, AP 00211-01A1, and the Petroleum Research Fund of the American Chemical Society, PRF-1247-A3, is gratefully acknowledged.

(8) A. S. Porter and F. C. Tompkins, *Proc. Roy. Soc. (London)*, **A217**, 529, 544 (1953).

(9) M. J. D. Low and H. A. Taylor, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **9**, 233 (1961).