

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY]

The Hydrogen-Deuterium Exchange Reaction on Zinc Oxide Catalysts

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The hydrogen-deuterium exchange reaction was investigated on zinc oxide samples, whose semi-conductivity was modified by the introduction of foreign cations into the zinc oxide lattice. The reaction follows kinetically two stages. During the first stage, characterized by increasing activity at constant temperature, the catalytic surface is being formed. The effect of preadsorbed oxygen on this stage is emphasized. During the second stage the catalytic activity and the activation energy of the reaction are affected by foreign additions to zinc oxide. The cation-anion ratio in zinc oxide determines the sign of the change in activity.

A considerable amount of experimental work has been centered on the elucidation of the electronic properties of zinc oxide.¹ These studies have shown that zinc oxide has a defective structure, stoichiometric unbalancing arising from the presence of an excess of the metallic constituent. The quasi-free electron concentration of the solid can be controlled by suitable adjustments of the cation-anion ratio, which determines the *n*-type semi-conductivity of the solid phase. The possibility therefore arises that a change in the electron concentration, within the same crystalline phase, may affect heterogeneous processes involving electron transfer or sharing with the solid phase. Such a situation presents itself in studies of chemical interactions, occurring at the surface of zinc oxide, whose bulk semi-conductivity is known to be modified by heterogeneous reactions.

In order to test these considerations, the exchange reaction between hydrogen and deuterium was investigated on a zinc oxide sample, whose semi-conductivity was modified by suitable additions of foreign ions.² In particular it was deemed interesting to investigate whether in the present case a relation could be established between the type of addition and the kinetics of the heterogeneous process, as previous work has shown to be the case for the reduction of nickel oxide,³ and the catalytic oxidation of carbon monoxide on nickel oxide.⁴ Recently Wagner⁵ tried to increase the activity of zinc oxide catalysts for the oxidation of carbon monoxide by incorporating in the lattice of zinc oxide 1 mole of gallium oxide. His expectation, however, was not fulfilled by the experimental results.

(1) D. J. M. Bevan, J. P. Shelton and J. S. Anderson, *J. Chem. Soc.*, 1729 (1948); D. J. M. Bevan and J. S. Anderson, *Discs. Faraday Soc.*, No. 8, 238 (1950); E. E. Hahn, B. R. Russell and P. H. Miller, Jr., *Phys. Rev.*, **75**, 1631 (1948); E. E. Hahn, *J. Appl. Phys.*, **22**, 855 (1951); R. Hirschberg and E. Lange, *Naturwissenschaften*, **39**, 187 (1952); C. A. Hogarth, *Phil. Mag.*, **39**, 260 (1948); *Z. physik. Chem.*, **198**, 30 (1951); E. Mollwo, *Ann. Physik*, [6] **3**, 230 (1948); E. Mollwo and F. Stockmann, *ibid.*, [6] **3**, 240 (1948); F. Stockmann, *Z. Physik*, **127**, 563 (1950); P. H. Miller, "Semiconducting Materials," Interscience Publishers, Inc., New York, N. Y., 1950, p. 172; G. Heiland, *Z. Physik*, **132**, 354, 367 (1952); H. Weiss, *ibid.*, **132**, 335 (1952); H. Fritzsche, *ibid.*, **138**, 422 (1952). The article by E. E. Hahn contains a rather comprehensive bibliography up to 1948.

(2) E. J. W. Verwey, P. W. Haayman and F. C. Romeijn, *Chem. Weekblad*, **44**, 705 (1948); E. J. W. Verwey, *Bull. soc. chim. France*, D93 (1949); E. J. W. Verwey, P. W. Haayman, F. C. Romeijn and G. W. Osterhout, *Philips Research Repts.*, **5**, 173 (1950); C. Wagner, *J. Chem. Phys.*, **12**, 62 (1950); K. Hauße, *Ann. Physik*, [6] **8**, 201 (1950); K. Hauße and A. L. Vierk, *Z. physik. Chem.*, **196**, 159 (1950); E. J. W. Verwey, "Semiconducting Materials," Interscience Publishers, Inc., p. 151.

(3) G. Parravano, *THIS JOURNAL*, **74**, 1194 (1952).

(4) G. Parravano, *ibid.*, **75**, 1448, 1452 (1953).

(5) C. Wagner, *J. Chem. Phys.*, **18**, 69 (1950).

Experimental

Materials and Apparatus.—C.P. zinc oxide (J. T. Baker) was used as manufactured (non-sintered zinc oxide) or was sintered for 3 hours at 800° in air (sintered zinc oxide). Alumina-, lithia- and gallia-containing samples were prepared by impregnation of the pure oxide with definite amounts of standard solutions of the corresponding nitrates. The impregnated materials were then dried at 110°, heated at 460° for 6 hours (non-sintered samples), or at 800° for 3 hours (sintered samples). Red zinc oxide containing 0.022% excess zinc, was prepared according to the method of Kutzelnigg⁶ and Ehret and Greenstone⁷ by heating a mixture of ammonium nitrate and zinc oxide (2:1) to the point of deflagration. The red zinc oxide formed was separated by elutriation with successive portions of distilled water. While this preparation of red zinc oxide produced a material which contained traces of NO₃⁻, in the red oxide activated in hydrogen at 230° (see below) no detectable traces of NO₃⁻ were found.

An electrolytic cell containing 30% water solution of potassium hydroxide was used to produce hydrogen, which was purified by passage through palladized asbestos, calcium chloride, magnesium perchlorate, and Ascarite. Deuterium was obtained by electrolysis of 99% D₂O, to which metallic sodium had been added. Deuterium was purified in a manner similar to hydrogen. Tank nitrogen, purified by passage over hot cooper, Ascarite, magnesium perchlorate and phosphorus pentoxide, and tank helium purified over active charcoal (-190°), hot copper, Ascarite, magnesium perchlorate and phosphorus pentoxide were used to measure nitrogen adsorption on zinc oxide samples. Chemisorption data were obtained with a standard type of apparatus.⁸ The kinetics of the hydrogen-deuterium reaction was followed in a flow system. A stream of hydrogen containing 2% deuterium flowed, at constant rate at atmospheric pressure, through the catalyst, contained in an electrically heated reactor, whose temperature was controlled by a manometric thermoregulator (±1°). After leaving the reactor, the reaction products were fed to a Nier-type mass spectrometer, directly connected with the flow system, and possessing two collectors. Mass spectrometric readings gave directly the ratio HD/H₂. Signals from both collectors were introduced into a feedback amplifier, which enabled part of the mass 2 signal to be used to cancel the potential of the mass 3 signal. The adjustment necessary to obtain this balance was taken as an indication of the ratio of the peak heights. A platinum catalyst was used to obtain the equilibrium composition of the H₂ + 2% D₂ mixture. In the case of lithia-containing samples kinetic data were obtained with the aid of a static system.⁹

Method of Measurement.—Nitrogen adsorption data were plotted according to BET theory in order to obtain surface areas of the zinc oxide samples. In previous studies of the present reaction on zinc oxide,^{10,11} it was found that the catalyst had to be submitted to a suitable treatment before any conversion could be detected. In the present work two different methods of pretreatment have been used: (a) at 450° in vacuum (10⁻⁶ Torr.) for 3.5¹⁰; (b) in hydrogen

(6) Kutzelnigg, *Z. anorg. allgem. Chem.*, **208**, 23 (1932).

(7) W. Ehret and A. Greenstone, *THIS JOURNAL*, **65**, 872 (1943).

(8) H. S. Taylor and S. C. Liang, *THIS JOURNAL*, **69**, 1306 (1947).

(9) For details see R. J. Mikovsky, Thesis, Princeton, 1951.

(10) E. A. Smith and H. S. Taylor, *THIS JOURNAL*, **60**, 362 (1938).

(11) V. C. F. Holm and R. W. Blue, *Ind. Eng. Chem.*, **44**, 107 (1952).

at temperatures up to 350° for 9 hours.¹¹ The activity of the resulting catalyst varied according to the type of pre-treatment. Kinetic data were computed from the percentage conversion

$$q = \left[\frac{(\text{HD}/\text{H}_2)_t}{(\text{HD}/\text{H}_2)_\infty} \right] \times 100 \cong [(\text{HD})_t/(\text{HD})_\infty] \times 100$$

where $(\text{HD}/\text{H}_2)_\infty$ refers to the equilibrium ratio. Values of q were determined at different flow rates (S.T.P.), and constant temperature. Values of flow rates and of the corresponding temperatures at a constant conversion value (see Fig. 3) were used to obtain the activation energies for the exchange reaction, according to the Arrhenius equation. This procedure was repeated for at least three different values of conversion. This method of determination of the activation energy is independent of the kinetic order followed by the reaction.

Results.—Surface area data for sintered and non-sintered samples are collected in Table I.

TABLE I
SURFACE AREA (M.², G.⁻¹) FOR SINTERED ZINC OXIDE SAMPLES

Sample	Surface area
ZnO	4.0 ^a
ZnO	1.6
ZnO + 0.022% Zn	0.5
ZnO + 1 mole % Al ₂ O ₃	3.5
ZnO + 1 mole % Ga ₂ O ₃	3.6
ZnO + 1 mole % Li ₂ O	0.12

^a Non-sintered.

A typical activation run for pure, non-sintered zinc oxide (per 1 sq. m. of surface) at constant temperature, 230°, using a flow of 0.119 cc. sec. of H₂ + 2% D₂ is presented in Fig. 1. It was found that activation data for this and similar runs on different samples could be fitted into the equation

$$dq/dt = ae^{-q\alpha} \quad (1)$$

with α , a , constants at constant temperature (Fig. 2). The following values for the initial rate a and the constant α were derived (Table II) for various catalysts.

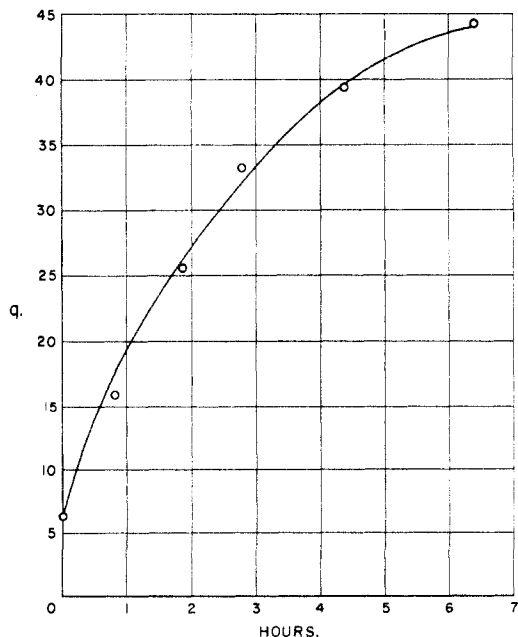


Fig. 1.—Activation of pure, non-sintered, ZnO (1 sq. m.) in H₂ + 2% D₂, 230°, flow rate 0.119 cc./sec.

Typical kinetic runs carried out at successively increasing temperatures on activated samples are recorded in Figs. 3 and 4. In the case of pure sintered zinc oxide different results were obtained if runs were carried out at successively

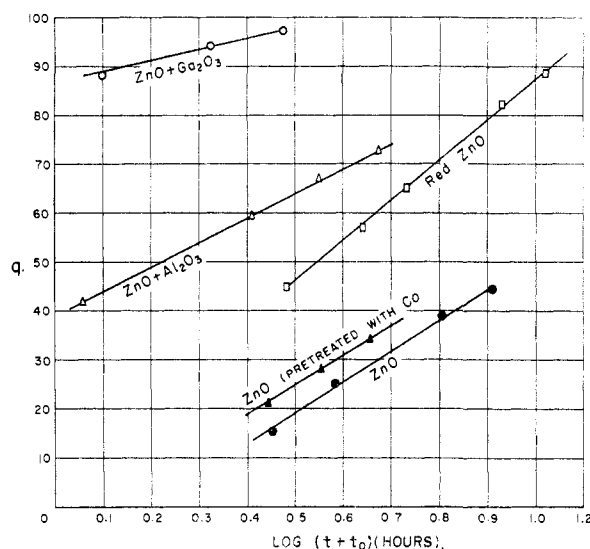


Fig. 2.—Plot of the integrated form of eq. 1 for treatment of ZnO samples (1 sq. m.) in H₂ + 2% D₂, flow rate 0.119 cc./sec.: ●, $t_0 = 2$, 230°; □, $t_0 = 2$, 231°; ▲, $t_0 = 0$, 231°; ○, $t_0 = 0$, 215°; ◆, $t_0 = 2$, 225°.

TABLE II
ACTIVATION OF SINTERED ZINC OXIDE SAMPLES IN H₂ + 2% D₂

Sample	Temp., °C.	a , min. ⁻¹	α
ZnO (non-sintered)	230	0.31	1.60
ZnO ^a	225	.30	1.65
ZnO + 0.022% Zn	231	.42	1.20
ZnO + 1 mole % Al ₂ O ₃	231	.25	2.00
ZnO + 1 mole % Ga ₂ O ₃	215	.20	4.15

^a Pretreated with CO at 230° for 3.5 hours, evacuated on cooling to room temperature, followed by admission of the H₂ + 2% D₂ mixture.

TABLE III
ACTIVATION ENERGIES, E , FOR THE HYDROGEN-DEUTERIUM EXCHANGE REACTION ON ZINC OXIDE CATALYSTS

Catalysts	Temp. range, °C.	E , kcal./mole
Non-sintered		
ZnO ^a	25-230	7.2 ± 0.5
ZnO + 1 mole % Al ₂ O ₃ ^a	25-185	5.0 ± 0.3
ZnO + 1 mole % Li ₂ O ^a	45-110	25.0 ± 3.0
ZnO + 0.022% Zn	40-170	5.0 ± 0.5
Sintered		
ZnO ^b	45-115	17.1 ± 1
ZnO ^b	115-170	~0
ZnO + 1 mole % Al ₂ O ₃ ^c	45-115	8.2 ± 0.5
ZnO + 1 mole % Al ₂ O ₃ ^c	115-170	~0
ZnO + 1 mole % Ga ₂ O ₃ ^b	45-115	6.3 ± 0.5
ZnO + 1 mole % Ga ₂ O ₃ ^b	115-170	~0
ZnO + 1 mole % Li ₂ O ^d	45-110	>25
ZnO + 1 mole % Li ₂ O ^d	110-160	18.0 ± 1.0

^a Activated in H₂ + 2% D₂ at 305°. ^b Activated under vacuum (450°) and H₂ + 2% D₂ at 170°. ^c Activated under H₂ + D₂ at 350°, cooled to 170° and left at this temperature for ~2 hours. ^d Activated at 350° in H₂ + 2% D₂.

increasing or decreasing temperatures. This effect is shown in Fig. 5. In Fig. 6 are presented the data obtained on non-sintered samples, containing foreign ions, pretreated in H₂ + D₂ at 305° and taken at increasing temperatures. Similar activity data were obtained on these samples from runs carried out at successively decreasing temperatures. The

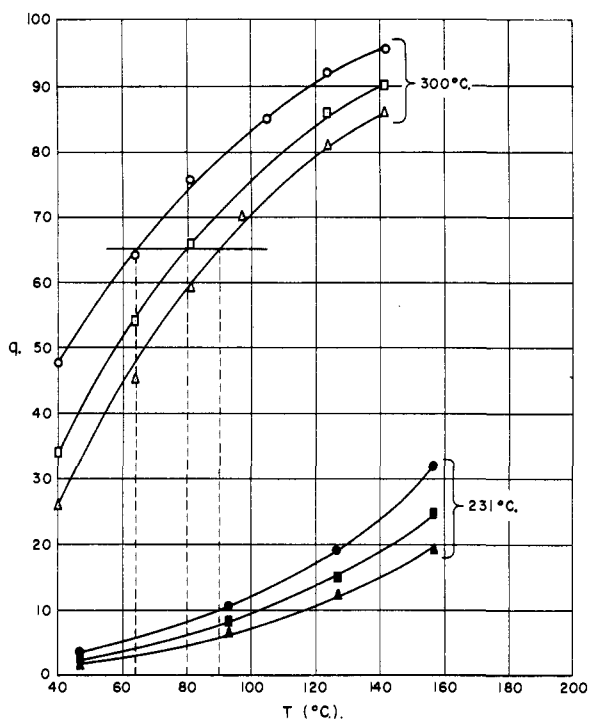


Fig. 3.— $\text{H}_2\text{-D}_2$ exchange on pure, non-sintered ZnO (1.66 sq. m.): Δ , \blacktriangle , flow rate 0.238 cc./sec.; \square , \blacksquare , flow rate 0.178 cc./sec.; \circ , \bullet , flow rate 0.119 cc./sec. Samples pretreated in $\text{H}_2 + 2\%$ D_2 at 231 and 300° . Dotted lines show method employed for the determination of the activation of the activation energies.

data obtained, at increasing temperatures on sintered samples, hydrogen activated at 230° and at 350° , are shown in Fig. 7. The activity of pure zinc oxide and zinc oxide + 1 mole % of gallia, both sintered and vacuum activated at 450° , are presented in Fig. 8. It was further found that activated samples, both in vacuum and hydrogen, could be deactivated by letting air or oxygen flow on the samples, which could again be reactivated following the usual procedure. Reproducible activity results could be obtained for sintered catalysts only after submitting the samples to an activation procedure which differed according to the samples treated. Under these conditions it was possible to derive the activation energies for different catalysts.

Hydrogen chemisorption on pure non-sintered, non-activated zinc oxide could not be detected at temperatures up to 300° , while hydrogen chemisorption could be readily measured on samples heated in vacuum at 400° overnight. These findings are in agreement with the work of Taylor and Sickman.¹²

Discussion

The present data indicate that the catalytic activity of zinc oxide for the hydrogen-deuterium exchange reaction can be varied by incorporation of solid additions to the zinc oxide lattice, and that the cation-anion ratio in zinc oxide which controls its defective structure is decisive in determining the direction of the change of the catalytic activity. Moreover, the data show that the exchange reaction proceeds through two different stages: (a) a first stage, kinetically described by equation 1, characterized by increasing activity, followed by (b) a second stage of constant activity. It is known that a large amount of chemisorbed oxygen is present on zinc oxide samples prepared in air,¹³ the resulting surfaces being more stoichio-

(12) H. S. Taylor and D. Sickman, *THIS JOURNAL*, **54**, 602 (1932).

(13) K. Hauffe and H. J. Engell, *Z. Elektrochem.*, **55**, 366 (1952).

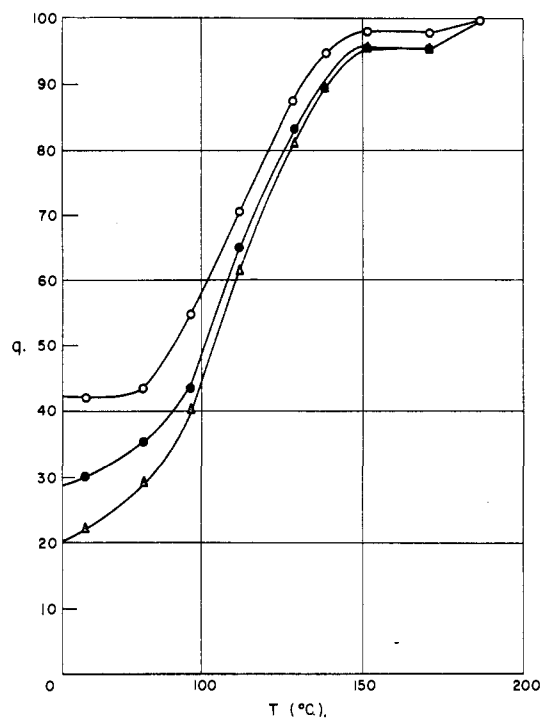
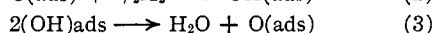
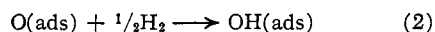


Fig. 4.— $\text{H}_2\text{-D}_2$ exchange on pure, non-sintered ZnO (2.34 sq. m.), pretreated in vacuum at 450° for 3.5 hours: \circ , flow rate 0.119 cc./sec.; \bullet , flow rate 0.178 cc./sec.; Δ , flow rate 0.238 cc./sec.

metric than the bulk. The precise bonding conditions of this chemisorbed oxygen are largely unknown. Hydrogen pretreatment of zinc oxide samples can be described as the reduction of adsorbed oxygen, *viz.*



Equations 2 and 3 are not confined to the surface, and further hydrogen adsorption can occur by a mechanism involving ionic migration or place exchange, under conditions where any lattice self-diffusion can take place. Such might be the case in a place exchange between a surface OH^- and an underlying O^{2-} from the lattice, as Roberts and Anderson¹⁴ recently suggested. This mechanism would account for the identical rates of hydrogen and deuterium chemisorption¹⁵ and, because of the almost identical size between O^{2-} and OH^- , for the fact that hydrogen chemisorption on zinc oxide does not affect its lattice parameter.¹⁶ Supporting evidence for the mechanism here proposed for the activation process can be obtained from the data on the pretreatment of zinc oxide samples with carbon monoxide and on the treatment with air of hydrogen activated samples. In the former case, although carbon monoxide pretreatment produces a reduction of the surface oxygen, the resulting surface carbonate or CO_3^{2-} complex is not active for the exchange reaction. Indeed, data from this laboratory¹⁷ have shown that at temperatures

(14) L. E. J. Roberts and J. S. Anderson, *Revs. Pure and Appl. Chem.*, **2**, 1 (1952).

(15) J. Pace and H. S. Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(16) L. Yang, *J. Electrochem. Soc.*, **97**, No. 4, 91c (1950).

(17) Unpublished results of Mr. L. A. Rheame.

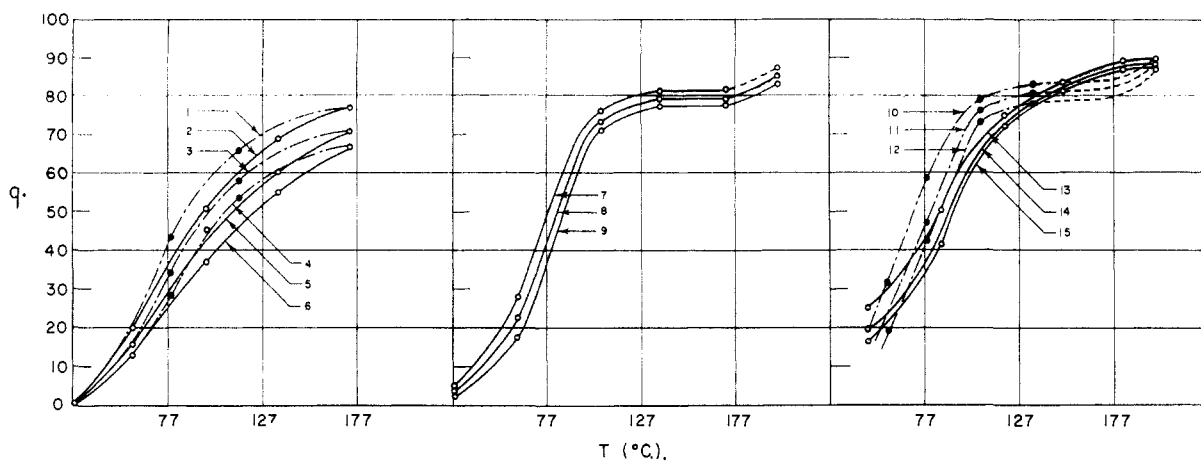


Fig. 5.— H_2 - D_2 exchange on pure, sintered ZnO. Curves 1-6 refer to samples hydrogen activated at 360° (0.175 sq. m.); 1, 2, flow rate 0.238 cc./sec.; 3, 5, flow rate 0.356 cc./sec.; 4, 6, flow rate 0.476 cc./sec.; 2, 5, 6, increasing temperature; 1, 3, 4, decreasing temperature. Curves 7, 8, 9 refer to samples hydrogen activated at 230° (1.04 sq. m.); 7, flow rate 0.119 cc./sec.; 8, flow rate 0.238 cc./sec.; 9, flow rate 0.356 cc./sec. Curves 10-15 refer to samples vacuum activated at 430° (1.04 sq. m.); 10, 13, flow rate 0.238 cc./sec.; 11, 14, flow rate 0.366 cc./sec.; 12, 15, flow rate 0.476 cc./sec.; 13, 14, 15, increasing temperature; 10, 11, 12, decreasing temperature.

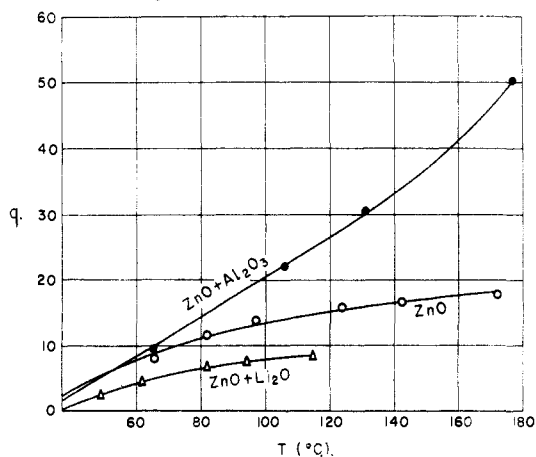


Fig. 6.— H_2 - D_2 exchange on non-sintered ZnO containing foreign ions (0.30 sq. m.), pretreated in hydrogen at 305° , flow rate 0.238 cc./sec.

$\leq 400^\circ$ zinc oxide does not catalyze the oxidation of carbon monoxide, suggesting that at these temperatures, the surface CO_3^{-2} complex is stable and acts as a poison for the oxidation reaction. On the other hand, air treatment of activated catalysts reoxidizes the hydrogenated surface compound, thus producing again an inactive, nearly stoichiometric surface. It should be emphasized also that the explanation here suggested for the activation of zinc oxide catalysts is quite general, and should apply to all cases of n -type semiconductors, prepared in oxidizing atmosphere, and used in a hydrogen atmosphere. Indeed, data of Holm and Blue¹¹ and unpublished results from this Laboratory show that several molybdenum, tungsten and uranium oxides and tungsten bronzes are not active for the hydrogen-deuterium exchange unless they are subjected to pretreatments similar to those used for zinc oxide. Since partial surface reduction is a necessary condition for catalytic activity, one may conclude that the catalytic reaction occurs by exchange between hydrogen or

deuterium and the surface OD or OH groups, respectively, as Wicke¹⁸ has already shown to be the case for the mechanism of the hydrogen-deuterium exchange reaction on alumina catalysts. Since surface hydroxyl groups are formed during stage (a) the measured catalytic activity will be found to increase with time during stage (a).

Variations in the activation energy of the catalytic reaction with temperature can be explained by assuming the presence of two different surface hydrogenated compounds. In this respect the present data on the temperature dependence of the activation energy closely parallel the results of Wicke¹⁸ for hydrogen chemisorption on zinc oxide. This author has shown that hydrogen chemisorption properties of zinc oxide varied anomalously at $\sim 100^\circ$. This fact led Wicke to propose that below 100° zinc sites are active for hydrogen chemisorption, while at higher temperatures the adsorption involves the formation of OH groups. It is interesting to note that only sintered catalysts show, in the range of temperature investigated, anomalies in the values of the activation energy as compared to non-sintered catalysts. Possibly upon sintering, the surface of zinc oxide becomes rich in excess zinc, thus resulting in a more pronounced low temperature mechanism for the exchange reaction.

The effect of the additions on the activation energy of the exchange reaction both for sintered and unsintered samples is difficult to explain. In fact, on the assumption that the measured activation energy refers to the desorption process,^{8,10} variation in the activation energy obtained by foreign additions to zinc oxide might arise from a change in the activation energy of adsorption and/or in the heat of adsorption. It is not possible from our data to decide the relative contributions of these two quantities. Separate measurements of both on these samples are needed. These results, however, are consistent with previous

(18) E. Wicke, *Z. Elektrochem.*, **53**, 279 (1949).

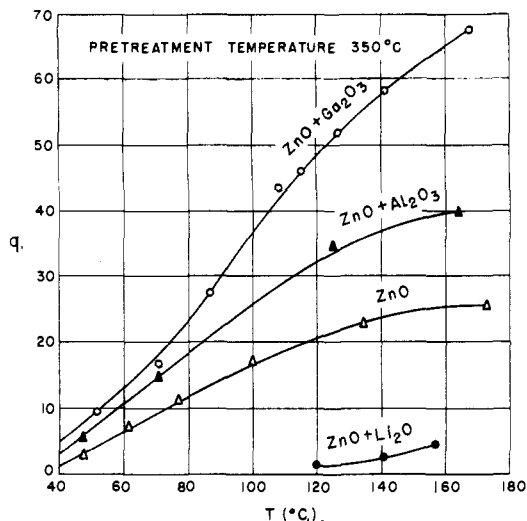


Fig. 7a.— H_2 - D_2 exchange on sintered ZnO containing foreign ions activated in hydrogen at 350° (0.1 sq. m.), flow rate 0.238 cc./sec.

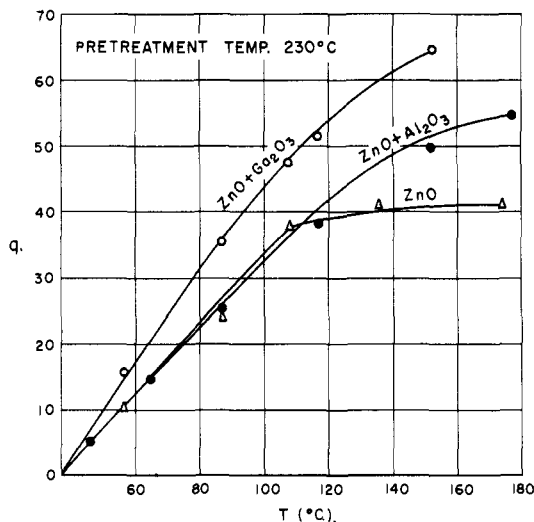


Fig. 7b.— H_2 - D_2 exchange on sintered ZnO containing foreign ions pretreated in hydrogen at 230° (1 sq. m.), flow rate 0.238 cc./sec.

work.^{3,4} In cases where the determining step of the heterogeneous process was the chemisorption of an electron donor (H_2 , CO), a more conducting solid phase was found to increase the activation energy of the process. In the present case this result might therefore be taken as supporting evidence for the Smith and Taylor¹⁰ conclusion as to the determining step of hydrogen-deuterium exchange reaction on zinc oxide. The effects that different impurities have on the sintering of zinc oxide can be explained in terms of the defective structure of the oxide. Surface migration, which is mainly responsible for sintering of oxide powders, occurs in oxides in

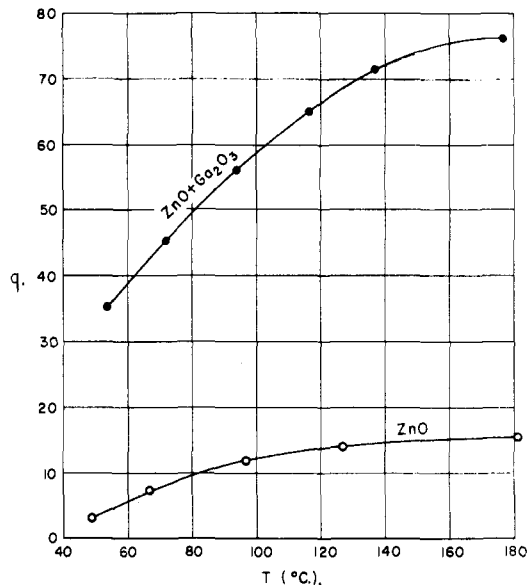


Fig. 8.— H_2 - D_2 exchange on sintered ZnO and ZnO + 1 mole % Ga_2O_3 (0.3 sq. m.), pretreated in vacuum at 450° and in H_2 + 2% D_2 at 170° , flow rate 0.238 cc./sec.

general through a mechanism involving ionic defects, and any factor which modifies the defective structure of the oxide will affect its sintering ability. In zinc oxide the ionic defects present are either interstitial zinc ions or anion vacancies. Both are decreased by additions of gallia or alumina to zinc oxide, and increased by introduction of lithia. Therefore sintering properties should be increased by addition of lithia and decreased by addition of gallia. This is remarkably shown by the values of surface areas presented in Table I.

Conclusions.—The exchange reaction between hydrogen and deuterium on zinc oxide occurs through the following steps: (1) The primary step is a truly surface reaction, which creates defects on the hitherto almost stoichiometric surface. These defects might be associated either with cations abnormally charged (Zn^+) or anions foreign to the lattice (OH^-). This is a slow activated process. The effect of the bulk on this primary step is reflected in the past history of surface formation. (2) The second stage is a truly catalytic reaction, whereby hydrogen is exchanged with the hydrogenated surface compound formed during stage (1). The heat of formation of the surface compound is paramount in determining its range of stability on the surface, and therefore the over-all catalytic activity of the latter at any temperature.

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