

STUDIES OF CHEMISORPTION OF HYDROGEN ON CERIC OXIDE

by S. K. BHATTACHARYYA*, F.N.A., V. SITAKARA RAO and K. S. DE,
Department of Chemistry, Indian Institute of Technology, Kharagpur-2, West Bengal

(Communicated by Prof. S. K. Bhattacharyya, F.N.A.)

(Received 12 March 1976; after revision 16 February 1977)

Chemisorption studies have been carried out on pretreated ceric oxide at different temperatures and pressures in an atmosphere of hydrogen. These studies reveal the presence of both weak and strong forms of hydrogen chemisorption. The weaker form predominates below 80°C which gradually changes to the stronger form at higher temperatures. The kinetics of chemisorption data obeyed Elovich equation. The influence of temperature and pressure on the Elovich parameters is discussed and the activation energy at zero coverage is calculated by the method of Allen and Scaife (1966). Results suggest a possible clustering of adsorbed molecules during hydrogen chemisorption.

INTRODUCTION

The catalytic properties of ceric oxide in the pure form (Rienacker & Wu 1962; Minachev & Khodakov 1965; Dimitur 1969; and Breysse *et al.*, 1972) in the form of mixed catalysts (Rienacker & Wu 1962; and Komarewsky & Wernik 1957) and in the form of promoters (Or & Orzechowskii 1952 *a, b*) in oxidation, dehydration and dehydrogenation reactions have been investigated extensively. The present work investigates the chemisorption characteristics and kinetics of chemisorption of hydrogen on variously pretreated ceric oxide under different conditions of temperature and pressure

EXPERIMENTAL

Ceric oxide was prepared by precipitating the hydroxide from ceric ammonium nitrate (A.R. B.D.H.) and then decomposing it at 450°C. DTA and TG studies showed that all the free and bound water molecules were thus completely removed. The oxide was activated by heating at the same temperature for about 6 hrs in a current of dry air. Chemical analyses showed that the product had a purity of about 99 per cent. X-ray diffraction studies confirmed the FCC structure with a lattice parameter of 5.416 Å. The specific surface area, as determined by the B.E.T. method using nitrogen as the adsorbate at -183.5°C. was 10.1 m²g⁻¹.

The gases used, viz., nitrogen and hydrogen, were purified by the usual standard methods.

The adsorption isotherms and the kinetics of chemisorption studies were carried out using the apparatus earlier described by Bhattacharyya *et al.* (1965). Briefly stated

*Present Address : Department of Chemistry, Faculty of Science, Banaras Hindu University Varanasi-221005.

about 8 g of catalyst (100 to 150 mesh size BSS) were taken in the catalyst tube and degassed at 500°C for 6 hrs using a two stage mercury diffusion pump backed by a rotary pump. The residual pressure obtained on evacuation was of the order of 10^{-5} to 10^{-6} mm Hg. The samples were protected from stop-cock grease and mercury vapour by using a liquid air trap. The temperature could be controlled and known with a precision of $\pm 1^\circ\text{C}$.

After evacuation, the catalyst tube was finally maintained at the required experimental temperature. Known quantities of hydrogen were then admitted at noted intervals, and after equilibration, the amounts of gas adsorbed (at N.T.P.) at different pressures were found from a knowledge of the gas left in the system. The adsorption experiments were carried out at 0°C, 27°C, 70°C, 100°C, 150°C and 200°C.

In kinetics experiments, about the same amount of ceric oxide was taken in a catalyst tube, adequate quantity of hydrogen was introduced into the system after the above evacuation procedure. Keeping the pressure in the system constant, the volume changes at different times, t , were noted. From the volume of the gas adsorbed at the temperature and pressure of the experiment, the volume, V , in ml of the gas adsorbed at N.T.P. per gram of the catalyst was calculated. The experiments were restricted in the temperature range 70°C to 200°C as the rate of adsorption was very small below 70°C, while at temperatures above 200°C, the rate of adsorption was rather high.

Computer programmes were used for finding out the correlation coefficients, which were an index of the goodness of fit of the experimental data to the various kinetic expressions as given by Aigrain and Dugas (1952); Bangham and Burt (1924); Ghosh *et al.* (1952); Kodama equation as given by Swamy (1969) and the generalised Elovich equation as given by Allen and Scaife (1966).

The Elovich equation, viz.,

$$\frac{dq}{dt} = a \exp. [-b(q - \nu q_0)]$$

where a , b , ν and q_0 are constants and q is the quantity of gas chemisorbed at time t , was tested by linear regression analysis. The correlation coefficient 'r' for a series of

values of k for the linear regression of V on $\log \left(\frac{t+k}{k} \right)$ was determined and the

best value of k was so chosen as to yield a maximum value of 'r.' If more than one kinetic stage was obtained graphically by plotting V vs. $\log t$, the optimum value of k for the first stage was determined using the computer and the various parameters of the Elovich equation for each stage were separately determined assuming that the value of k for the first stage was applicable throughout.

RESULTS AND DISCUSSION

Isotherms for adsorption of hydrogen on ceric oxide were obtained at temperatures in the range 0° to 200°C and pressures upto 120 mm Hg. Adsorption isobars at typical pressures are presented in Fig. 1. A minimum around 80°C suggests two

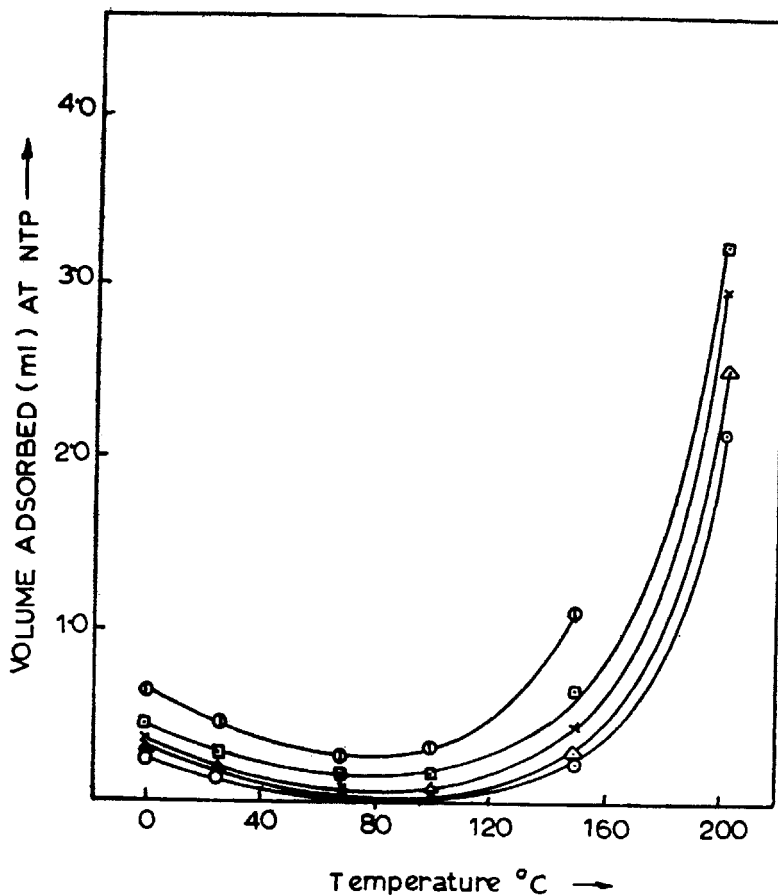


FIG. 1. Hydrogen adsorption isobars on ceric oxide.

⊙—⊙—⊙ 8 cm Hg; □—□—□ 5 cm Hg; ×—×—× 4 cm Hg;
 △—△—△ 3 cm Hg; ⊙—⊙—⊙ 2.5 cm Hg.

types of adsorption processes—a weaker chemisorption at lower temperatures which gradually changes over to a stronger form at higher temperatures.

Kinetics of chemisorption were studied at 70°, 100°, 150° and 200°C at pressures in the range 100 to 500 mm Hg. Typical results at 100° and 150°C are presented in Fig. 2; similar results were obtained at other temperatures. For a given time interval, the volume of the gas adsorbed increases, in general, both with increase in pressure and temperature, as expected. The data were analysed using kinetic schemes of Elovich; Bangham-Burt; Kodama; Ghosh *et al.* (1952); and Aigrain and Dugas (1952). From the correlation coefficients, the generalised form of Elovich equation in the form given by Allen and Scaife, viz.,

$$\frac{dq}{dt} = a \exp. [-b(q - v q_0)]$$

appeared to fit the data better. V vs. $\log t$ plots (not shown) indicated that two or three kinetic schemes could be recognised. Typical V vs. $\log(t+k)$ plots are shown in Fig. 3; similar plots were obtained at other temperatures. Parameters of the Elovich equation from these plots are given in Table I. The breaks in the Elovich plots can

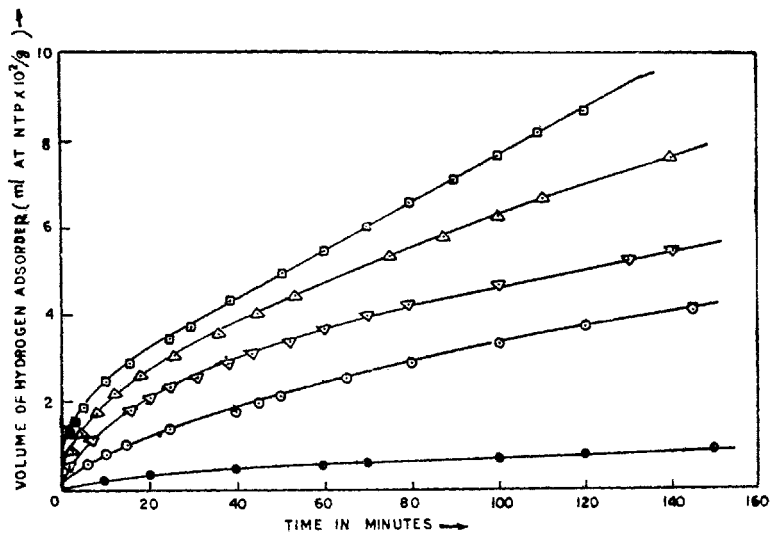


FIG. 2. Kinetics of hydrogen chemisorption on ceric oxide at 100°C and 150°C. At 100°C: ●—●—● P = 11.5 cm Hg; ○—○—○ P = 21.5 cm Hg; ▽—▽—▽ P = 30.8 cm Hg; △—△—△ P = 52.4 cm Hg. At 150°C: □—□—□ P = 31.0 cm Hg.

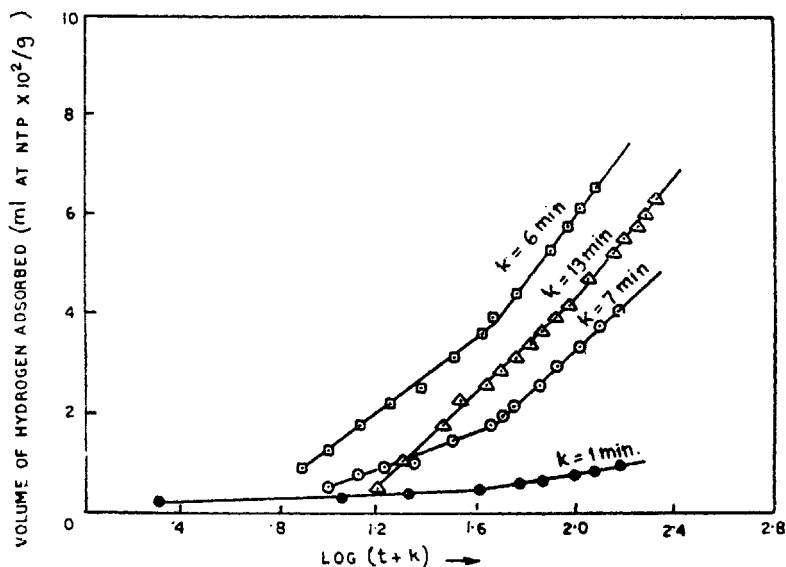


FIG. 3. Elovich plots for hydrogen chemisorption on ceric oxide at 100°C. ●—●—● P = 11.5 cm Hg; ○—○—○ P = 21.5 cm Hg; ▽—▽—▽ P = 30.8 cm Hg; □—□—□ P = 52.4 cm Hg.

TABLE I
Parameters of the generalized Elovich equation

Expt. No.	Temperature (°C)	Pressure (cm Hg)	k	$10^2 q_0$ (ml NTP)	$10^2 a_I$ (min ⁻¹)	b_I	$10^2 a_{II}$ (min ⁻¹)	b_{II}	$10^2 a_{III}$ (min ⁻¹)	b_{III}
1	70	30.7	3.5	0.15	0.12	242.8				
2	70	39.9	14.0	0.77	0.15	138.8				
3	70	52.0	4.0	0.71	0.22	112.2				
4	100	11.5	1.0	0.22	0.19	521.6	0.40	249.8		
5	100	21.5	7.0	0.22	0.10	138.6	0.28	51.0		
6	100	30.8	13.0	0.22	0.15	50.5	0.21	37.5		
7	100	52.4	6.0	0.40	0.27	61.1	0.56	30.0		
8	150	31.0	10.0	1.12	0.19	53.6	0.46	21.8		
9	200	12.2	16.0	0.09	0.28	22.7	0.76	8.2		
10	200	21.2	20.0	1.35	0.75	6.6	0.82	6.1		
11	200	31.9	18.0	0.23	0.93	5.9	0.17	3.3		
12	200	40.5	3.0	0.32	2.48	13.4	6.77	4.9	11.77	2.8
13	200	52.6	4.0	0.05	2.46	10.1	5.36	4.7	9.95	2.5

Subscripts, I, II and III refer to the values for kinetic stages first, second, and third respectively.

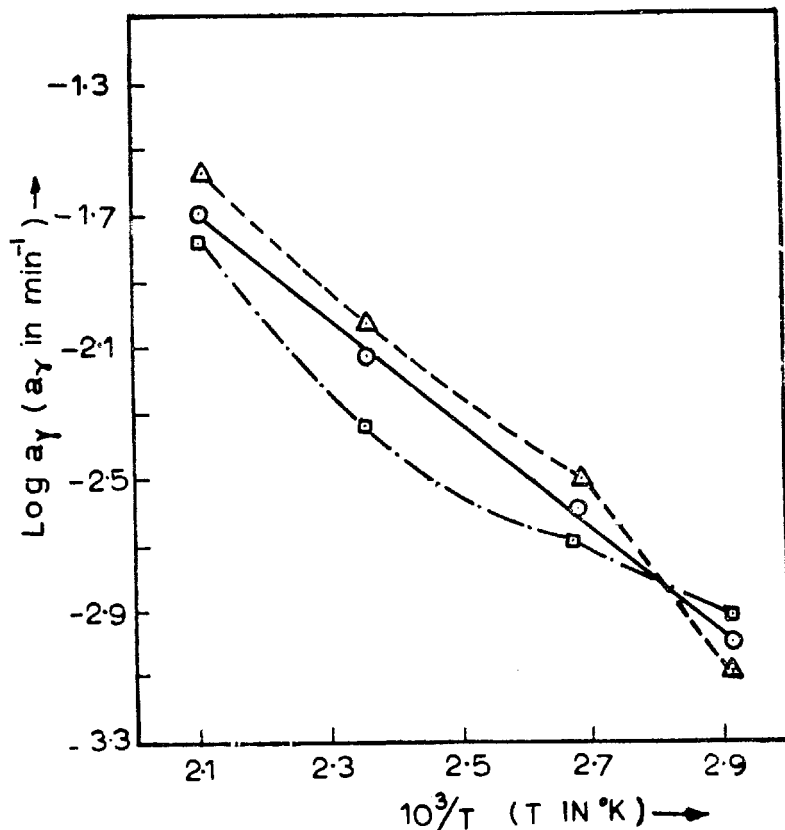


FIG. 4. Temperature dependence of rate of adsorption at $q=0$ (at a pressure of 30 cm Hg for temperatures 70°C to 200°C). $\Delta-\Delta-\Delta$ $v = 1.0$; $\circ-\circ-\circ$ $v = 1.5$; $\square-\square-\square$ $v = 2.0$.

TABLE II
Activation energy at zero coverage for the chemisorption of hydrogen on ceric oxide

Sl. No	Kinetic stage	Pressure (cm Hg)	Value of ν	Activation energy (kcal mole ⁻¹)
1	1	30	3.0	7.04
2	1	50	3.0	8.96
3	2	30	1.5	7.49
4	2	50	1.5	7.86
				Mean value = 7.84

be interpreted due to a change of one kind of sites to the other during adsorption. It will be noted that variation in the value of initial adsorption q_0 does not follow any trend indicating a continuous change of sites in the temperature range studied. Non-linear relationships for the constant 'b' for the first stage and I/T is also indicative of the changes in the nature of adsorption sites (Low & Taylor 1959; and Low 1960 *a, b*). Parameter 'a', which is a measure of the initial rate of adsorption, increases with increase in temperature at constant pressure.

The activation energy, as calculated from the plots of $\log t$ vs. $1/T$ using Arrhenius equation, is found to increase linearly with surface coverage. This clearly points out to the energetic heterogeneity of the adsorbent surface.

The activation energy at zero coverage has been calculated by the method of Allen and Scaife (1966). Plots of $\log a$ vs. $1/T$, for the various values of ν (1.0, 1.5 and 2.0), are drawn for the kinetics of chemisorption of hydrogen at a pressure of 30 cm Hg in the temperature range 70°C to 200°C (Fig. 4). A linear fit is obtained only for $\nu = 1.5$. Using this value of ν , the corresponding activation energy (E) at zero coverage was calculated from the slope of the plot. The activation energies at zero coverage for a_I and a_{II} at 30 cm and 50 cm Hg have been also calculated in a similar manner and are presented in Table II. The value of ν is greater than 1 in all the cases which is indicative of an interaction of the adsorbed molecules with the neighbouring sites and formation of clusters around any single adsorption site.

The occurrence of kinetic multiplicity as indicated by the breaks in Elovich plots may be considered to arise from surface contamination, the heterogeneity of the adsorbent surface and the existence of multiple adsorbent adsorbate structures.

REFERENCES

- Aigrain, P. R., and Dugas, C. R. (1952). Adsorption on semiconductors. *Z. Elektrochem.*, **56**, 363-366.
- Allen, J. A., and Scaife, P. H. (1966). The Elovich equation and chemisorption kinetics. *Austr. J. Chem.*, **19**, 2015-2023.
- Bangham, D. H., and Burt, F. P. (1924). The behaviour of gases in contact with glass surfaces. *Proc. R. Soc.*, **105**, A, 481-488.
- Bhattacharyya, S. K., De, K. S., Pandao, S. N., and Chandrasekhar, G. V. (1965). Chemisorption and electrical conductivity studies on alumina-zinc oxide catalysts. *Proc. 3rd. int. Congr. Catal.*, **1**, 474-483.

- Breysse, M., Guenin, M., Claudel, B., Latreille, H., and Veron, J. (1972). Catalysis of carbon monoxide oxidation by cerium dioxide. Correlation between catalytic activity and electrical conductivity. *J. Catal.*, **27**, 275-280.
- Dimitur, K. (1969). Oxidation of methyl alcohol to formaldehyde on cerium dioxide. *Z. Chem.*, **9**(10), 394-396.
- Ghosh, J. C., Sastri, M. V. C., and Kini, K. A. (1952). Adsorption of hydrogen and carbon monoxide and their mixtures by Cobalt Fischer-Tropsch catalysts. *Ind. Engng. Chem.*, **44**, 2463-2470.
- Komarewsky, V. I., and Wernick, M. (1957). Catalytic properties of the rare earths. *Proc. Congr. intern. Chim. pure et Appl.*, 16e Paris, 249-255.
- Low, M. J. D. (1960a). Kinetics of chemisorption of gases on solids. *Chem. Rev.*, 267-312.
- (1960b). Rates of adsorption of hydrogen on palladium and on rhodium. *Can. J. Chem.*, **38**, 588-595.
- Low, M. J. D., and Taylor, H. A. (1959). The kinetics of hydrogen chemisorption on irridium catalyst. *Can. J. Chem.*, **37**, 915-921.
- Minachev, Kh. M., and Khodakov, Yu. S. (1965). Catalytic activity of the rare earth elements in the conversion of butane. *Kinet. Catal.*, **6**, 89-94.
- Or, L. D., and Orzechowskii, A. (1952a). Promotion in heterogeneous catalysis. *C. r.*, **235**, 368-370
- (1952b). Further studies on promotion in heretogeneous catalysis. *C. r.*, **235**, 430-432.
- Rienacker, G., and Wu, J. (1962). Effect of additives on oxide catalysts. XI. Properties of Cerium-Lanthanum mixed oxides especially as catalysts for the oxidation of carbon monoxide. *Z. anorg. allg. Chem.*, **315**, 121-135.
- Swamy, C. S. (1969). Kinetics of chemisorption of hydrogen on iron-kieselguhr : application of the equation of Kodama *et al.* *Curr. Sci.* **38**(12), 286-287.