analysis indicate a greater concentration of anion vacancies and free electrons in catalyst I than in catalyst II. The concentration of V^{4+} ions in catalyst I is 2% while that in catalyst II is 1%. These V^{4+} ions may play some part in methanol chemisorption but the nature of this is difficult to define.

References

1. Bhattacharyya, S. K., and Gulati, I. B., *Ind. Eng. Chem.* **50**, 1719 (1958).
2. Bhattacharyya, S. K., and Venkatraman, N., *J. Appl. Chem.* **8**, 728, 735 (1958).
3. Bhattacharyya, S. K., and Ganguli, N. D., *J. Indian Chem. Soc.* **38**, 463 (1961).
4. Bhattacharyya, S. K., and Mahanti, P., *Proc. Int. Congr. Catal., 4th,* Moscow, pap. No. 1, 23 (1968).
5. Bhattacharyya, S. K., and Mahanti, P., *J. Catal.* **12**, 20 (1971).
6. Bhattacharyya, S. K., De, K. S., Pandao, S. N., and Chandrasekhar, G. V., *Proc. Int. Congr. Catal., 3rd,* **1964**, 474 (1965).

S. K. Bhattacharyya
P. Mahanti

Department of Chemistry,
Banaras Hindu University,
Varanasi-5, India; and*
Indian Institute of Technology,
Kharagpur, India
Received May 19, 1971

* Present address.

Pressure Effects on the Elovich Kinetics*

Introduction

In the earlier paper (*1*), kinetics of hydrogen chemisorption on nickel–alumina catalysts were analyzed using the Elovich equation, viz.,

$$dq/dt = a \cdot \exp(-\alpha q) \qquad (1)$$

where q is the amount of gas adsorbed at time t, and a and α are constants, and a detailed study of the influence of temperature and initial pressure on the Elovich parameters was made. The present note deals with the effect of prevailing gas pressure on the rate of hydrogen chemisorption on nickel–alumina catalyst. Before doing experiments involving changes in the prevailing gas pressure, the catalyst was studied for its general adsorption behavior for the parameters a and α, and for the reproducibility of the surface at different temperatures and initial pressures (*1*).

Experimental

Adsorption measurements were carried out in a constant volume adsorption system, provided with a McLeod gauge and accurately calibrated mercury manometers. The nickel–alumina catalyst used in this study is the same "Catalyst 2" reported earlier (*1*) with a BET surface area of 118 m^2/g, and a metal surface area of 12.09 m^2/g.

Purification of gases, dead space determination, and the general kinetics experiments were carried out following the procedure described earlier (*1*). Changes in the prevailing gas pressures were brought about at the time t_c, after the onset of slow adsorption (i) by addition, (ii) by removal of a certain quantity of gas, keeping the volume of the system constant, and (iii) by cutting off a certain volume of the adsorption system during adsorption.

Results and Discussion

Effect of Initial Pressure

The effect of initial pressure on the Elovich parameters was studied at 30 and 200°C and the results are plotted in Fig. 1. Both α_1 and α_2, the α values for the kinetics stages 1 and 2, respectively, in-

---

* This work was done at the Chemistry Department of Loyola College, Madras 34, India.

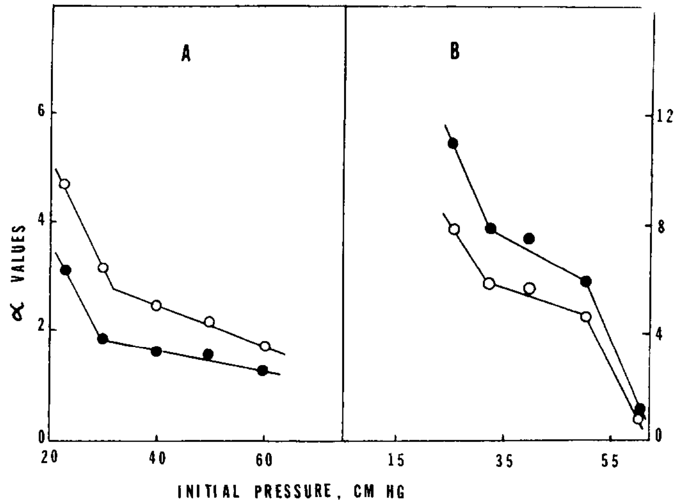

FIG. 1. Effect of initial pressure A: at 30°C; B: at 200°C. ○ α_1, ● α_2.

crease with the decrease of pressure, and the increase is significant at low pressures, around 23 cm Hg. Such an increase in the α values at low pressure regions was reported earlier (*1*, *2*). At 30°C, α_2 is less than α_1 whereas at 200°C α_2 is greater than α_1.

Low (*3*) derives the Elovich equation as an extension of Taylor's treatment, viz.,

$$dq/dt = k[V_o] \exp(-k_d q/k), \tag{2}$$

giving the values,

$$a = k[V_o], \tag{3}$$

$$\alpha = k_d/k, \tag{4}$$

k_d being the rate governing the site destruction process, but the site density itself is governed by the availability of $[V]$ which is dependent on $[H]$, in the site generation process. At low pressures, $[V]$ will be smaller, making k, the rate, smaller, thereby increasing the value of α, as experimentally observed with decrease in pressure.

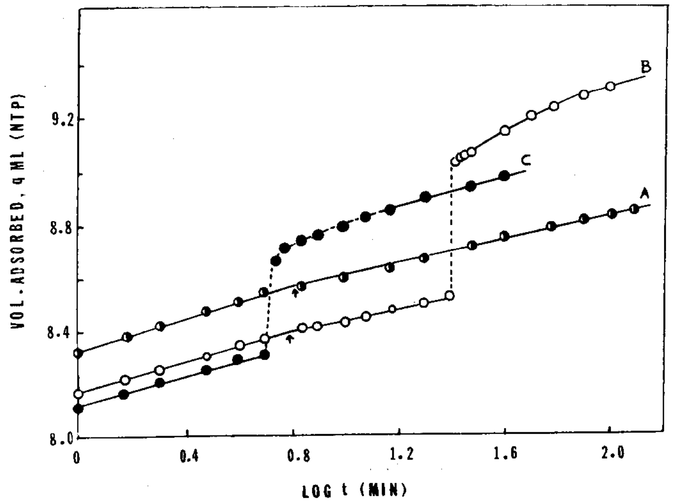

FIG. 2. Effect of prevailing gas pressure: Gas addition experiments at 200°C and 33 cm Hg. A: Normal run; B and C: Interrupted runs.

TABLE 1
Gas Addition Experiments at 200°C

Run	t_c (min)	α_1	α_2	$+\Delta p$ (cm Hg)	$+\Delta q$ (ml NTP)	$\frac{\Delta q}{\Delta p} \times 10^2$	t_b	Δt
At Initial Pressure 33 cm Hg								
2.21	Normal	7.62	9.63	—	—	—	7	—
2.28	25	7.62	9.63	37.8	0.89	2.36	7	—
2.29	25	7.45	9.49	21.3	0.50	2.35	6	—
2.31	5	6.42	—	13.4	0.40	3.02	—	10
2.32	6	7.49	—	27.6	0.86	3.11	—	14
2.33	6	—	—	25.0	0.99	3.18	—	14
At Initial Pressure 26 cm Hg								
2.22	Normal	9.63	12.83	—	—	—	6	—
2.44	5	—	—	27.9	0.93	3.33	—	—
2.45	5	—	—	20.9	0.84	4.06	—	—
2.46	40	9.63	—	21.0	0.76	3.64	7	—

Effect of Changes in the Prevailing Gas Pressure

Gas addition experiments were carried out at two pressures, viz., 33 and 26 cm Hg and at 200°C. Figure 2 represents the Elovich plots for the gas addition experiments, where *A* represents the normal run, *B* and *C* the interrupted runs. The interruptions were made after the occurrence of the break in *B* and before the appearance of the break in *C*. The plots show a sudden increase in the amount adsorbed, Δq, corresponding to the increase in pressure Δp, in the system. In some experiments it was not possible to determine exactly the time of occurrence of the break.

The results of the gas addition experiments are given in Table 1 and the $\Delta q/\Delta p$ ratio shows some constancy. t_b is the time of occurrence of the break and Δt is the time interval after which the Elovich plots of the interrupted runs become parallel to the plot of the normal run.

A set of gas removal experiments was carried out at 30°C and initial pressure 60 cm Hg and the results are summarized in Table 2 showing a constancy in $\Delta q/\Delta p$ ratio. Figure 3 shows the plots for the gas removal experiments. Plot *A* represents the normal run and the plots *B*, *C*, and *D*, the interrupted runs where different amounts of gases were removed before and after the occurrence of breaks. It is also evident from the plots *B*, *C*, and *D* that an immediate desorption occurs as a result of the removal of gas and only after an interval of time Δt, do the plots of the interrupted runs become parallel to the plots of the normal run. Moreover, the time of occurrence of the breaks in the interrupted runs is increased as a result of the gas removal.

In the case of run 2.27 (Plot 3*B*), gas

TABLE 2
Gas Removal Experiments at 30°C and 60 cm Hg

Run	t_c (min)	α_1	α_2	$-\Delta p$ (cm Hg)	$-\Delta q$ (ml NTP)	$\frac{\Delta q}{\Delta p} \times 10^2$	t_b	Δt
2.30	Normal	2.76	2.22	—	—	—	7	—
2.24	6	—	2.22	4.40	0.36	8.27	20	6
2.26	6	—	2.03	14.80	1.13	7.62	40	8
2.27	20	2.89	—	21.80	1.63	7.68	7	—

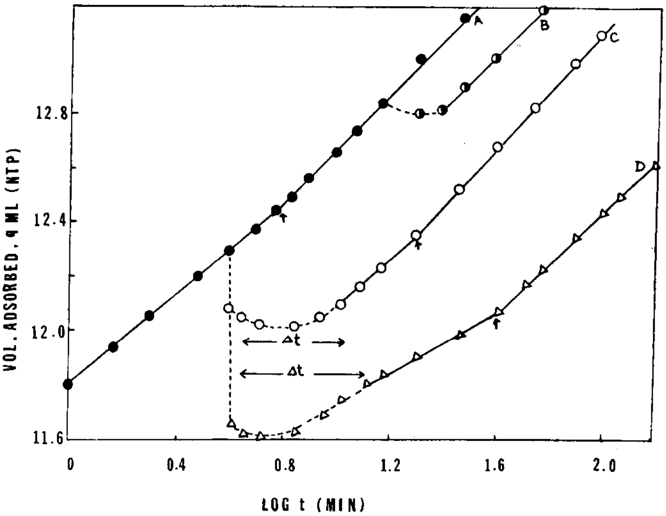

FIG. 3. Effect of prevailing gas pressure: Gas removal experiments at 200°C and 60 cm Hg. *A*: Normal run; *B*, *C*, and *D*: Interrupted runs.

was removed at the 20th minute and the plot is parallel to the corresponding portion of plot 3*A* thereby indicating that α_2 values are independent of the ambient pressure.

In the interrupted runs the burette portion was cut off at the 5th minute and reconnected at the 50th minute. Figure 4 represents the Elovich plot for the normal run along with the plot for the interrupted run. Both portions of the two plots are parallel to each other and the breaks occur in the same direction around the same time irrespective of the interruption.

It was observed that changes in the prevailing gas pressures have no influence on α value once the slow adsorption had set in which is in agreement with Taylor–Thon mechanism (*4*) as well as Gundry–Tompkins mechanism (*5*) of chemisorption.

Taylor *et al.* (*6*) reported no systematic

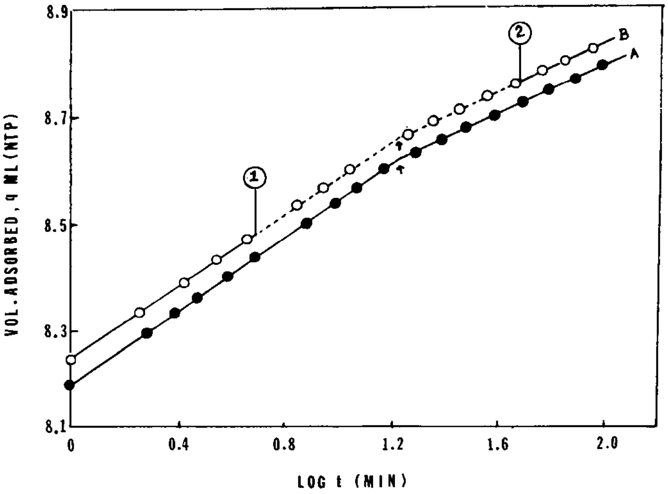

FIG. 4. Effect of prevailing gas pressure. *A*: Normal run *B*: Interrupted run. ① Burette cut off; ② Burette reconnected.

variation of Δq which is a measure of rapid adsorption or desorption following the addition or removal of gas and offered no explanation for the phenomenon. However, the present investigation reveals that Δq is dependent on Δp and is independent of the time at which the pressure change was brought about. In the gas removal experiments the instantaneous desorption is much more than what was taken up slowly in that stage and is not characteristic of the adsorption stage. This has been reported earlier on nickel–magnesia–hydrogen system (*7*). These observations indicate the possibility of the desorption taking place from the initial fast adsorption, before the onset of slow adsorption. This can be explained on the basis of Gundry–Tompkins mechanism: When the pressure change is made during the slow adsorption by the addition or removal of gas, the rapid adsorption or desorption, i.e., $\pm \Delta q$ takes place in or from the intermediate Type C state. Since the concentration of hydrogen atoms in the intermediate state is determined solely by the initial pressure of hydrogen, there is necessarily a direct proportionality of Δq to Δp.

From Taylor–Thon point of view, the chemisorption at any instance is controlled by the site density V. V is formed by a generation process formulated as

$$H + S = HV + V \qquad (5)$$

where S is any active point on the surface (*3*). Since in this process the amount of V is stoichiometrically controlled by H, removal of hydrogen from the zone of adsorption should decrease V as substantiated by the constancy of the $\Delta q/\Delta p$ ratio referred to earlier.

It is suggested that after the addition or removal of gas there is a slow adsorption or desorption accompanying the rapid process, $\pm \Delta q$, and this process extends over the interval Δt. Consequently during the time Δt, the normal adsorption ± the slow process takes place. After Δt, the slow process ceases and the normal rate alone continues thereafter as shown by the parallelism of the plots.

In the gas removal experiments, the time of occurrence of the break is shifted farther (Table 2) and this shift varies directly with Δp. Because the slow desorption probably takes from the intermediate state so that after gas removal more time is needed to fill this desorbed amount and for the break to occur.

In the present investigation the pressure effects on the adsorption kinetics were carried out at fairly high initial pressures such as 26, 33, 40, and 60 cm Hg. However, it might be very interesting and useful to study the prevailing pressure changes at very low initial pressures since at low pressures the effect of a small change in the ambient pressure on the kinetics of adsorption will be appreciable.

REFERENCES

1. Narayanan, S., and Yeddanapalli, L. M., *J. Catal.* **21**, 356 (1971).
2. Viswanathan, N. S., and Yeddanapalli, L. M., *Can. J. Chem.* **47**, 2933 (1969).
3. Low, M. J. D., *Chem. Rev.* **60**, 267 (1960).
4. Taylor, H. A., and Thon, N., *J. Amer. Chem. Soc.* **74**, 4169 (1952).
5. Gundry, P. M., and Tompkins, F. C., "Chemisorption," Proc. Symposium, Keele, p. 152. Butterworths, London, 1957.
6. Leibowitz, L., Low, M. J. D., and Taylor, H. A., *J. Phys. Chem.* **63**, 471 (1958).
7. Ramasubramanian, N., and Yeddanapalli, L. M., *J. Phys. Chem.* **66**, 1222 (1962).

S. Narayanan

Department of Chemistry
St. Joseph College
West Hartford
Connecticut, 06117

Received September 7, 1971