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Kinetics of Hydrogen Adsorption on Nickel–Alumina Catalysts

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Kinetics of hydrogen chemisorption on four coprecipitated nickel–alumina catalysts have been studied at a variety of temperatures and pressures. The Elovich equation has been used to analyze the experimental results. The Elovich parameters obtained at different temperature and pressure regions are arranged according to the multiple kinetic stages hypothesis by Low and a plausible explanation on the nature of the active sites on nickel–alumina catalysts for hydrogen chemisorption is given.

INTRODUCTION

Because the electronic structure of the solid is important in chemisorption, it is to be expected that its effect will be implicit in any expression for the rate of chemisorption. Many attempts to represent the kinetic data by algebraic mass action functions involving integral or fractional powers of concentration, or by partial pressure of gas and constant rate parameters, or definite order have not been successful. However, a complete survey of literature shows that one form of kinetic expression, viz.,

$$dq/dt = a \cdot \exp(-\alpha q), \tag{1}$$

where q is the amount of gas adsorbed at time t, and a and α are constants, seems to have a wide and general applicability to chemisorption data (*1*). This expression, commonly known as the Elovich equation is mostly used in the integrated form,

$$q = 1/\alpha[\ln(t + t_0) - \ln t_0], \tag{2}$$

where $t_0 = 1/a\alpha$.

It is interesting to note that the Elovich rate law is not too sensitive to the nature of the gas or to the nature of the surface. Also, several different approaches to the mechanism of chemisorption have resulted in the logarithmic rate law, so that the Elovich equation can no longer be regarded as a purely empirical formulation. Consequently, the Elovich equation has been adopted in our present study to express the rate data on a nickel–alumina–hydrogen system. The present study is an extension of our earlier work on a nickel–magnesia–hydrogen system (*2–4*), where we found evidences for the multiple kinetic stages postulated by Low (*1*). In our recent paper we have also reported activation energies for the first three stages (*4*). Preliminary studies made on the adsorption of hydrogen on nickel–alumina catalysts (*5*) also substantiated our earlier results. A more detailed investigation on the kinetics of hydrogen chemisorption on four coprecipitated nickel–alumina catalysts has been reported in this paper.

EXPERIMENTAL

Apparatus and Materials

The adsorption studies were carried out using a conventional constant-volume adsorption system, provided with a McLeod gauge and accurately calibrated mercury manometers.

The adsorbent was prepared by coprecipitating the mixed hydroxide from a solution of nickel nitrate and aluminium nitrate by the addition of 1 N sodium hydroxide.

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The precipitate, after washing well with distilled water, was dried at 110°C for 12 hr, and finally the dried hydroxides were reduced in a stream of pure hydrogen. By varying the percentages of nickel content, the time, and the temperature of reduction, four samples of nickel–alumina catalysts were prepared. The specifications of some of the catalysts used in the present study have been reported elsewhere (*6, 7*). Table 1 summarizes the properties of the catalysts.

Procedure

Dead space measurements were made with nitrogen according to the method described by Lobenstein (*8*). Hydrogen and nitrogen from tanks were purified by following the procedure described earlier (*7*), and the purified gases were stored in bulbs.

Between adsorption measurements, the adsorbent was degassed for 8 hr at 380 ± 4°C at 10^{-6} cm Hg, using Cenco Megavac and mercury diffusion pumps along with cold traps. The reproducibility of the surface measurements was checked by repeating the adsorption experiments at standard conditions.

In the present study, the plot of q vs log t (Elovich plot) was a straight line and the linearizing constant t_0 was found to be small, hence the algebraic method of Sarmousakis and Low (*9*) was used throughout for the evaluation of the Elovich parameters.

Using the integrated form of the Elovich equation, viz.,

$$(q_{nt} - q_{mt}) = (2.3/\alpha) \log n/m, \qquad (3)$$

where q_{nt} and q_{mt} are the amount of gas adsorbed at time nt and mt, respectively, and α can be calculated. Knowing α from Eq. 3, a can be calculated using the known values of q from the equation,

$$q = (2.3/\alpha) \log a\alpha. \qquad (4)$$

RESULTS

From the review by Low (*1*) on the kinetics of chemisorption of gases by solids, one can see that in a number of gas–solid systems the Elovich plots (q vs log t) showed changes both in direction and magnitude, and each portion of the plot can be characterized by its own parameters a and α. With the systems hydrogen-palladium and hydrogen-rhodium, Low (*10*) could detect more than two kinetic stages in a single experiment, and on that basis he postulated multiple kinetic stages for adsorption. The Elovich plots for the adsorption of hydrogen on nickel–alumina indicated the presence of more than one kinetic stage (*5, 11*). In order to find a possible explanation for the multiple kinetic stages and also to test its universality, detailed experiments were carried out. In analyzing our kinetic data, we assume the presence of multiple kinetic stages and try to explain our results on that basis.

TABLE 1

SPECIFICATIONS OF THE CATALYSTS USED IN THE EXPERIMENTS

Specification	Catalysts 1	2	3	5
Wt % of nickel content (by analysis)[a]	30.1	30.1	30.1	50.8
Weight of catalysts (g)	3.59	4.10	4.13	5.06
Weight of nickel in the catalysts (g)	0.743	0.84	0.854	1.41
Reduction temperature (°C)	390	490	390	390
Reduction time (hr)	12	12	72	72
BET surface area (m^2/g)[b]	163.7	118.0	155.1	81.4
Metal surface area (m^2/g)[c]	8.74	12.09	12.27	7.53

[a] Estimated by DMG method and electroanalysis, base alumina = 100.

[b] Using nitrogen as the adsorbate at −183°C.

[c] From hydrogen adsorption isotherm at 19°C.

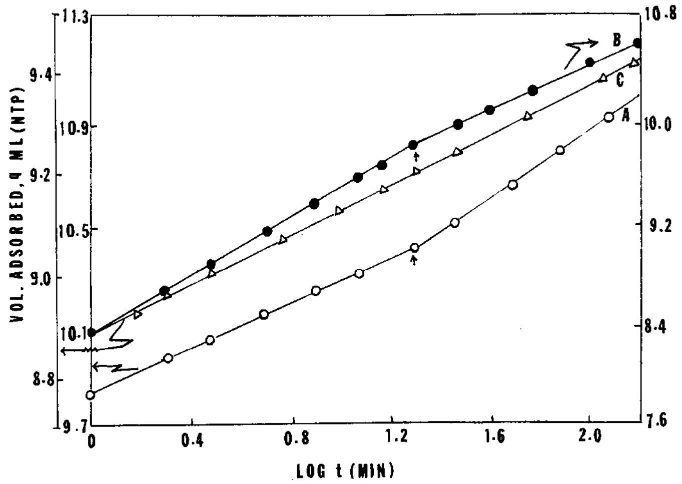

FIG. 1. Elovich plots on Catalyst 1, where pressure = 60 cm Hg; Plot A at 200°C; plot B at 30°C; and plot C at 135°C.

Influence of Temperature

Kinetic measurements were made on all the four catalysts at a variety of temperatures and pressures in order to find the influence of temperature and pressure on the Elovich parameters.

Figures 1 and 2 represent the general Elovich plots at different temperatures on catalysts 1 and 2, respectively. In plot 1B, the break occurs around the 25th minute, and the slope of the first segment of the plot is higher than the slope of the second segment of the plot. In other words, α_1 is less than α_2, where 1 and 2 represent the first and second segments of the plot, and α equals 1/slope. On the other hand, the Elovich plot 1A is different from 1B, and the break appears around the 20th minute. In this case, the slope of the first segment of the plot is lower than the slope of the second segment, i.e., α_1 is greater than α_2. However, plot 1C is just a straight line.

The effect of temperature on the Elovich parameters is summarized in Table 2. All the runs were carried out at 60 cm Hg, the maximum variation in the initial pressure being 1.5%. As has been mentioned

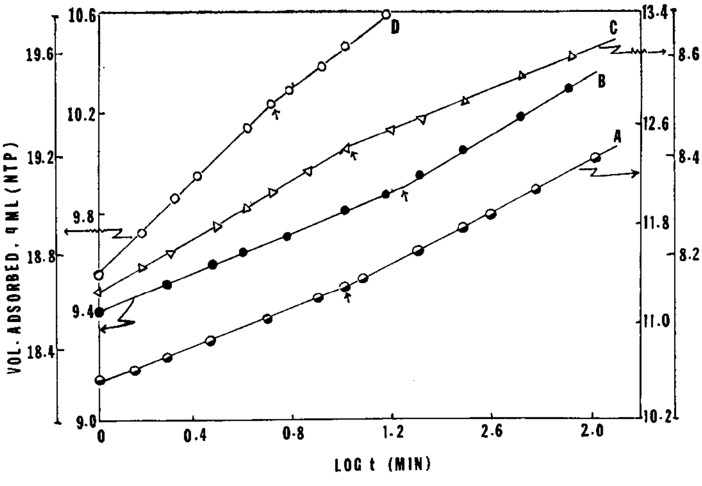

FIG. 2. Elovich plots on Catalyst 2; plot A at 30°C and 60.15 cm Hg; plot B at 30°C and 23.15 cm Hg; plot C at 200°C and 26.32 cm Hg; and plot D at 200°C and 59.67 cm Hg.

TABLE 2
EFFECT OF TEMPERATURE ON ELOVICH PARAMETERS AT 60 CM HG

Run	Temp (°C)	α_1	α_2	α_3	a_1	a_2	a_3	t_b
					Catalyst 1			
1.2	200	5.73	3.67	—	5.32×10^{23}	1.08×10^{16}	—	20
1.3	190	7.30	6.13	—	9.74×10^{27}	2.28×10^{24}	—	21
1.13	180	7.97	6.48	—	3.89×10^{27}	3.54×10^{22}	—	23
1.11	150	9.90	7.70	—	4.89×10^{30}	6.22×10^{30}	—	25
1.19	135	6.10	6.10	6.10	4.30×10^{22}	4.30×10^{22}	4.30×10^{22}	—
1.18	130	—	4.96	5.98	—	1.70×10^{17}	3.20×10^{19}	—
1.8	90	—	3.94	4.81	—	2.60×10^{14}	1.70×10^{19}	—
1.6	30	—	2.11	3.04	—	2.11×10^{7}	3.37×10^{12}	—
					Catalyst 2			
2.4	200	—	2.57	2.95	—	2.88×10^{20}	—	—
2.5	180	—	4.15	5.02	—	6.33×10^{25}	—	—
2.6	160	—	4.53	5.21	—	7.65×10^{26}	—	—
2.7	140	—	3.52	4.31	—	2.11×10^{20}	—	—
2.8	120	—	2.86	3.79	—	7.61×10^{16}	—	—
2.9	100	—	2.81	3.14	—	2.14×10^{16}	—	—
2.10	80	—	2.47	2.67	—	1.85×10^{11}	—	—
2.12	30	2.76	2.22	—	9.30×10^{11}	—	—	—
2.13	0	2.45	1.92	—	7.26×10^{9}	—	—	—
					Catalyst 3			
3.1	200	—	4.99	6.30	—	6.06×10^{26}	2.95×10^{35}	—
3.3	30	—	2.16	—	—	3.59×10^{11}	—	—
					Catalyst 5			
5.2	200	—	5.02	5.77	—	3.62×10^{22}	—	—
5.5	0	1.93	1.58	—	3.55×10^{6}	—	—	—

earlier in this section, the results are analyzed according to the multiple kinetic-stage mechanism. On the basis of the observation made by Low on the kinetics of chemisorption, there is a justification in comparing these parameters only in the region where the same kinetic stages are observed all through. On that basis, if one compares the Elovich parameters in the case of Catalyst 1, one sees that α_1 is always greater than α_2 in the temperature region 150–200°C. Both α_1 and α_2 decrease with the increase of temperature, which is normal. However, the a values also decrease with the increase of temperature, which is anomalous. This type of decrease in a and α with temperature has been observed in the case of nickel–magnesia–hydrogen system (*12*) and also in the case of nickel–kieselguhr (*13*). The nickel–alumina–hydrogen system falls under the (α–, a–) group of Low's classification (*1*) in the temperature region 150–200°C. Moreover, the a value is very sensitive, and even a small variation in q will affect a to a large extent, and hence the fluctuation in a. The last column t_b represents the time of occurrence of break, in other words, the time at which the Elovich plot changes its slope, or it indicates the end of one kinetic stage and the beginning of a new kinetic stage. Increase of temperature always seems to help the early disappearance of one kinetic stage and the appearance of a new kinetic stage.

The variation of α with temperature is plotted in Fig. 3. The two plots for α_1 and α_2 intersect around 137°C. Around this temperature the α's should be equal and the Elovich plot a straight line, and this determined by carrying out a number

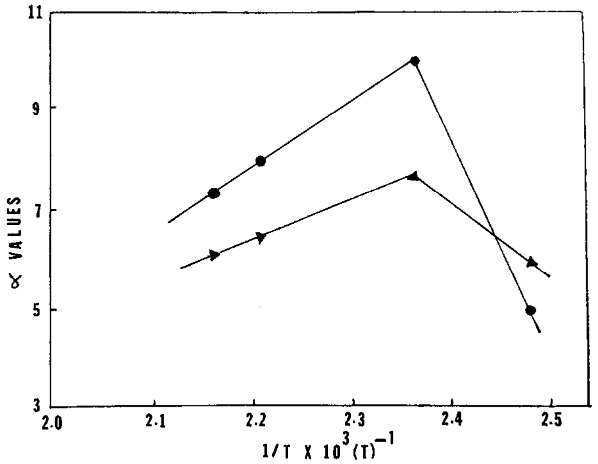

FIG. 3. Variation of α with temperature, Catalyst 1; ● = α_1, and ▲ = α_2.

of experiments in the region 130–150°C, and the exact temperature was found to be 135°C. Plot 1C represents the Elovich plot at this temperature.

Below 135°C the α_2 is always less than α_3, and the α values decrease with decrease of temperature instead of an increase.

Figure 2 represents the nature of the

TABLE 3

EFFECT OF PRESSURE ON ELOVICH PARAMETERS AT LOW TEMPERATURE[a]

Run	Pressure cm Hg	α_1	α_2	α_3	a_1	a_2	a_3	t_b
					Catalyst 1			
1.6	61.05	—	2.11	3.04	—	2.11×10^7	3.37×10^{12}	25
1.23	50.17	—	2.49	3.07	—	1.64×10^7	5.75×10^{11}	20
1.28	40.12	—	2.75	3.09	—	1.29×10^7	6.08×10^9	17
1.25	29.96	—	2.77	3.09	—	7.81×10^6	3.27×10^9	15
1.26	19.60	4.13	3.56	—	7.81×10^9	2.47×10^9	—	7
					Catalyst 2			
2.12	60.15	2.76	2.22	—	9.30×10^{11}	—	—	—
2.15	50.28	3.23	2.65	—	6.33×10^{12}	—	—	—
2.16	39.92	3.43	2.63	—	3.27×10^{14}	—	—	—
2.17	30.25	4.10	2.87	—	1.34×10^{17}	—	—	—
2.18	23.15	5.78	4.13	—	2.08×10^{22}	—	—	—
					Catalyst 3			
3.3	60.00	2.16	—	—	3.59×10^{11}	—	—	—
3.8	50.00	2.56	—	—	1.55×10^{13}	—	—	—
3.9	40.00	—	1.89	2.38	—	1.04×10^9	7.62×10^{11}	12
3.10	20.00	—	2.83	3.15	—	1.95×10^{14}	3.65×10^{21}	10
					Catalyst 5			
5.5	60.00	1.93	1.58	—	3.55×10^6	—	—	—
5.6	50.00	2.64	1.68	—	1.09×10^8	—	—	—
5.7	40.00	3.85	2.93	—	1.03×10^{12}	—	—	—
5.8	30.00	1.59	1.28	—	1.73×10^4	—	—	—

[a] Catalysts 1, 2, and 3 at 30°C and Catalyst 5 at 0°C.

Elovich plots on catalyst 2 obtained at two temperatures. Again, in the case of Catalyst 2, in the temperature region 80–200°C, α_2 is always less than α_3. From the parameters given in Table 2, for Catalyst 2, one can say that the temperature region 80–140°C is an anomalous region, since in this region, the α values increase with temperatures instead of an expected decrease. However, a values show an expected increase in this region. Above 140°C, the changes in α values are normal. Thus the effect of temperatures on the Elovich parameters in the ascending (80–140°C) as well as in the descending (160–200°C) regions of the isobar fall under (α–, a–) classification as in the case of Catalyst 1.

An examination of Table 2 shows that in the case of Catalyst 1, the kinetic stages I and II appear in the temperature region 150–200°C, and in the case of Catalysts 2 and 5, they appear in the region 0–30°C. In all the catalysts, kinetic stages II and III appear at all other temperature regions studied.

Influence of Pressure

In order to find out the effect of initial pressure on the Elovich parameters, a number of experiments were carried out on all the four catalysts in the pressure range 20–60 cm Hg. Tables 3 and 4 give a summary of the results of the experiments carried out at low and high temperatures.

An examination of Tables 3 and 4 reveals that with the decrease of pressure there is always a slight increase in the value of α and a. It is also interesting to note that t_b value also decreases with the decrease in pressure, i.e., with the decrease in initial pressure, the disappearance of a particular kinetic stage and the appearance of a new kinetic stage is facilitated.

Figure 4 represents the Elovich plots for

TABLE 4

EFFECT OF PRESSURE ON ELOVICH PARAMETERS AT HIGH TEMPERATURE (200°C)

Run	Pressure (cm Hg)	α_1	α_2	α_3	a_1	a_2	a_3	t_b
					Catalyst 1			
1.2	59.40	4.73	3.67	—	5.33×10^{23}	1.07×10^{11}	—	20
1.20	50.10	—	12.16	18.25	—	1.43×10^{46}	6.92×10^{71}	14
1.21	39.62	—	12.25	18.25	—	7.45×10^{41}	2.79×10^{62}	6
1.22	29.67	—	12.32	18.25	—	2.02×10^{40}	1.02×10^{61}	6
1.29	24.95	—	12.38	18.74	—	6.67×10^{32}	7.34×10^{51}	5
					Catalyst 2			
2.4	59.67	—	2.57	2.95	—	2.88×10^{20}	—	—
2.19	50.69	—	6.36	7.70	—	4.86×10^{28}	—	—
2.20	40.38	—	7.62	9.50	—	3.66×10^{30}	—	—
2.21	32.62	—	7.62	9.63	—	5.35×10^{26}	—	—
2.22	26.32	—	9.63	12.83	—	9.92×10^{32}	—	—
					Catalyst 3			
3.1	60.00	—	4.99	6.30	—	6.06×10^{26}	2.95×10^{35}	8
3.7	50.00	—	5.68	7.79	—	8.42×10^{28}	1.94×10^{39}	7
3.5	40.00	—	5.82	8.78	—	2.98×10^{29}	9.05×10^{49}	6
3.6	20.00	—	7.62	11.55	—	3.78×10^{35}	3.44×10^{60}	5
					Catalyst 5			
5.2	60.00	—	5.02	5.77	—	3.62×10^{22}	—	—
5.10	50.00	—	6.73	7.62	—	5.65×10^{17}	—	—
5.11	40.00	—	8.06	10.05	—	1.84×10^{15}	—	—
5.12	30.00	—	2.11	3.37	—	9.89×10^{11}	—	—

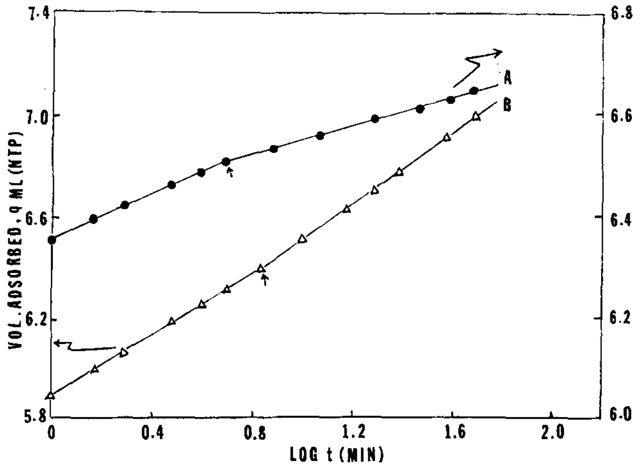

FIG. 4. Elovich plots on Catalyst 1. Plot A at 200°C; pressure, 24.95 cm Hg; and plot B at 30°C; pressure, 19.60 cm Hg.

the adsorption of hydrogen on Catalyst 1 at low pressures. Plots 4A and B can be treated as involving the kinetic stages II and III and I and II, respectively.

Figure 5 represents the variation of α with pressure. It is evident from the figure and also from the α values given in Table 3 for Catalyst 1 at 30°C that the variation is very smooth, and one does not see a drastic change in the α values with pressure, except at low pressure. The drastic change in the α value at low pressure can be seen from the examination of the α values for Catalysts 2 and 3 at 200°C. Also, from Table 4 one can see that except in the case of Catalyst 1 at 59.40 cm Hg (where stages I and II appear) in all the other cases, stages II and III are appearing. However, the analysis of Table 3 shows the presence of different kinetic stages in all the catalysts depending on the pressure.

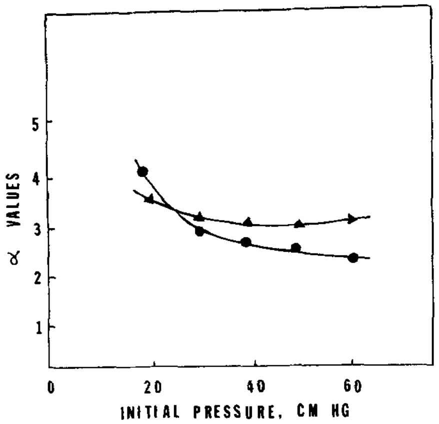

FIG. 5. Variation of α with pressure at 30°C, Catalyst 1; ● = α_1; and ▲ = α_2.

DISCUSSION

In the case of catalysts like the ones used in the present investigation where the catalysts are prepared by the reduction of mixed oxides, one would expect two types of adsorption, viz., fast and slow adsorption taking place on the catalyst surface. The amount of gas adsorbed at the first minute (q_1) is assumed to represent the fast adsorption, and the slow adsorption is indicated by the difference in the amount of gas adsorbed at the 100th minute and the first minute ($q_{100} - q_1$), assuming that the adsorption after the 100th minute is negligible.

An examination of the Elovich plots in Figs. 1, 2 and 4 will reveal that most of the total adsorption has occurred at the first minute (log $t = 0$), which accounts for about 80% of the total adsorption. The occurrence of fast and slow adsorption on nickel may be explained on the basis of the assumption that more than one type of adsorption site is present on nickel (*14*, *15*). It may also be possible that the environment of the nickel itself can be of importance in distinguishing the fast and

TABLE 5
SUMMARY OF THE RESULTS

Conditions of temperature and pressure	Catalysts 1	 2	 3	 5
High temperature and high pressure	I and II $\alpha_1 > \alpha_2$	II and III $\alpha_2 < \alpha_3$	II and III $\alpha_2 < \alpha_3$	II and III $\alpha_2 < \alpha_3$
High temperature and low pressure	II and III $\alpha_2 < \alpha_3$	II and III $\alpha_2 < \alpha_3$	II and III $\alpha_2 < \alpha_3$	II and III $\alpha_2 < \alpha_3$
Low temperature and low pressure	I and II $\alpha_1 > \alpha_2$	I and II $\alpha_1 > \alpha_2$	II and III $\alpha_2 < \alpha_3$	I and II $\alpha_1 > \alpha_2$
Low temperature and high pressure	II and III $\alpha_2 < \alpha_3$	I and II $\alpha_1 > \alpha_2$	— —	I and II $\alpha_1 > \alpha_2$

slow adsorption processes. The initial fast adsorption may occur on the pure surface nickel atoms, and this process may take place at very low coverages probably involving little or no activition energy. The subsequent slow adsorption would require high activation energy which would increase with coverage. Based on Gundry–Tompkins model (*16*) for chemisorption kinetics, one can consider the slow adsorption as an activated transition from Type C to Type A state. In this process, the different kinetic stages postulated by Low may be occurring at different heights in the potential energy level of Type A state.

The results of our experiments on the effect of temperature and pressure on the Elovich parameters are summarized in Table 5, and here again the results are arranged according to the multiple kinetic-stage picture (Fig. 6).

In the case of Catalyst 1, the Elovich plots for high temperature–high pressure and low temperature–low pressure runs are of the same type (α_1 is greater than α_2), whereas at high temperature–low pressure and low temperature–high pressure, the Elovich plots are of different type (α_2 is less than α_3). Different kinetic stages in the Elovich plots appearing at different temperature and pressure regions may be visualized as involving any two of Low's multiple kinetic stages (Fig. 6). By comparing the various plots for Catalyst 1 (Figs. 1 and 4) with the multiple kinetic stages in Fig. 6, one can say that the high temperature–high pressure and low temperature–low pressure adsorptions involve stages I and II, and high temperature–low pressure and low temperature–high pressure adsorptions involve stages II and III.

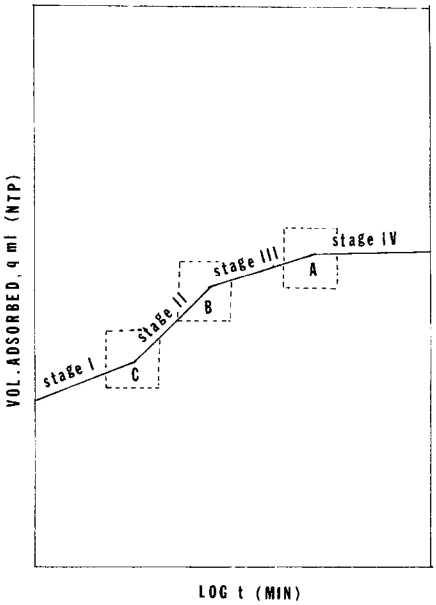

FIG. 6. Multiple kinetic stages, Low (*1*).

From Table 5, one finds that in the case of Catalyst 2, at high temperature and high pressure, stages II and III appear, and at low temperature and low pressure, stages I and II appear, which is different from what we have noticed in the case of Catalyst 1.

Catalyst 3 behaves entirely different

from Catalysts 1 and 2 in the same conditions of temperature and pressure. At all temperature and pressure regions, only stages II and III appear.

Again, Catalyst 5 was found to behave differently from Catalysts 1, 2, and 3. In this case, stages I and II appear at low temperature–low pressure and low temperature–high pressure regions, and the stages II and III appear at high temperature–high pressure and high temeprature–low pressure regions.

This raises the question whether the sites conceived for Catalyst 1 are present at all on the other samples and whether a multiple kinetic-stages diagram (Fig. 6) is possible to cover all the samples. If this is not possible, it would appear that we will have at least two different sites for each of the five catalysts, and since these were not chosen with any real knowledge of their behavior beforehand, we are left with the picture of innumerable sites—a whole spectrum of activities.

Of the number of mechanisms proposed for the kinetics of chemisorption, the Taylor–Thon model (*17*) takes into account the appearance of breaks in the Elovich plots. They suggested that if α was characteristic of the nature of the sites involved in the adsorption, then the break in the Elovich plots indicated a change over from one kind of site to another at a certain stage of the adsorption.

If it is so, the four stages in the multiple kinetic stages may be visualized as having four sets of sites, each set being homogenous in itself, and each set having its own activation energy. Our results, reported earlier (*4*), on the activation energy of adsorption for different kinetic stages seem to support this hypothesis. Depending on the conditions of temperature and pressure, a particular set of sites becomes activated.

With these systems, it is probable to come across more than four stages of adsorption, in other words more than four sets of active sites, all stages appearing in any one run. However, because of the limitations imposed by the techniques used and by the experimental variables of temperature and pressure, not all stages necessarily appear. Hence, one can easily explain the kinetics of chemisorption assuming the presence of four or five sets of active sites, each set having its own activation energy and the activation energy increasing with the amount of gas adsorbed (*18*). Depending on the conditions of temperature and pressure, a particular set of sites will get activated.

Tompkins *et al.* (*19*) have proposed a 'combined model' by postulating a patch wise heterogeneity of the adsorbent surface with additional induced effects on each homogeneous patch.

So far, several mechanisms and models have been proposed to explain the validity of Elovich equation, and also several criticisms have been raised. In spite of the criticism people continue to use, this simple kinetic equation and it seems to fit in very well. The wide applicability of the Elovich equation itself has caused less optimistic comment (*1*). The choice of a particular mechanism has always been one's preference, and probably with the accumulation of more data on the kinetics of chemisorption, one might be able to come out with a model which would be of physical significance and general applicability.

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