

STUDIES ON ULTRA-CLEAN CARBON SURFACES—III. KINETICS OF CHEMISORPTION OF HYDROGEN ON GRAPHON

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Abstract—The chemisorption of hydrogen on activated Graphon was studied over the range 80–600°C at a hydrogen pressure of 0.10 Torr and at 500°C over the pressure range 0.020–0.47 Torr. The Graphon was activated by preoxidation in oxygen to 18.6 per cent weight loss at 625°C. The oxidized sample had a BET surface area of 100 m²/g. Prior to adsorption measurements, the sample was outgassed at 1000°C at residual pressures < 10⁻⁸ Torr. Adsorption was followed for times up to 24 hr. Plots of amount of hydrogen adsorbed vs. log of time showed linear regions. In all, four linear regions were identified. The activation energy for chemisorption changed little within a linear region. However, it changed abruptly between linear regions, increasing over-all from 5.7 kcal/mole for the first linear region to 30.4 kcal/mole for the last. It is concluded that each linear region represents chemisorption on different discrete configurations of sites on the carbon surface.

I. INTRODUCTION

The interaction of hydrogen and carbon is one of the more important surface reactions and has engaged the attention of a number of workers. Bangham and Stafford [1], studying the adsorption of hydrogen on graphite, observed that large amounts of hydrogen atoms, and not molecules, were adsorbed at room temperature. They found that hydrogen-treated graphite became a good adsorbent for oxygen. This was attributed to the formation of ethylenic linkages on treatment of the graphite with hydrogen.

Barrer and co-workers [2, 3], while studying the adsorption of hydrogen on diamond and graphite, also observed that hydrogen is adsorbed as atoms and that the same atoms always desorbed to give back the hydrogen molecule. The activation energy for hydrogen chemisorption was found to be between 22 and 33.8 kcal/mole, as fractional surface coverage was increased from zero to about 0.3.

Kingman [4, 5] studied chemisorption of hydrogen on Norit, a highly purified charcoal. He found that hydrogen was not adsorbed at a measurable rate below 200°C. Over the temperature range from 340 to 395°C, the energy of activation of chemisorption was 30 kcal/mole in the range of 0–0.3 cc hydrogen per g of charcoal.

Burchstein, Levin and Petrov [6], while studying the adsorption of several gases on ash-free charcoal and charcoal containing 0.2% Pt, found that the charcoal containing platinum adsorbed hydrogen at 20°C but slow activated adsorption on ash-free charcoal did not occur until 400°C. The amount adsorbed was proportional to the square root of pressure; and for short time intervals, the rates of adsorption were proportional to the square root of time.

On the basis of studies relating to adsorption of oxygen, hydrogen and carbon dioxide on active charcoal surfaces and from the interpretation given by other workers,

Keier and Roginsky[7] postulated a new approach to the kinetics of adsorption. A statistical theory of adsorption was developed, which was applied to determine the distribution of active sites on these surfaces.

Thomas[8], while studying the adsorption of hydrogen on outgassed graphite, observed it to be an activated process in the temperature range 600–750°C. The activation energy for adsorption varied between 10 and 33 kcal/mole for fractional coverages between 0.10 and 0.60.

Redmond and Walker[9] studied the sorption of hydrogen on selected types of nuclear and spectroscopic graphite over the temperature range 920–1495°C. They found the isotherms to be of the Temkin type. However, at temperatures of 1085°C and above the isotherms consisted of two straight line regions of markedly different slopes. No firm explanation for the change in slope was proposed but it was suggested that the change may be due to surface heterogeneity. From kinetic studies on nuclear graphite between 1335–1495°C, the activation energy change with coverage (θ) was approximated by $E = 79 + 14(\theta)$ kcal/mole. They concluded that the adsorption of hydrogen occurs on carbon atoms at the edges of crystallites and that significant absorption of hydrogen interstitially between the basal planes of graphite does not occur.

A brief resume of the literature shows that: (1) chemisorption of hydrogen has not been carried out on well cleaned carbon surfaces and (2) sufficient kinetic data are not available in the literature to warrant the postulation of a definite mechanism for the interaction. As the carbon–hydrogen interaction is of fundamental importance in a number of processes where carbon and graphite are used, it seemed desirable to investigate the kinetics of the reaction using ultra-clean carbon surfaces.

It has been shown in Parts I and II of this series[10, 11], which were concerned with chemisorption of oxygen, that the Graphon

surface has discrete types of sites on which chemisorption takes place. Over the temperature range –78 to 160°C and at pressures between 7×10^{-4} and 7.6×10^2 Torr, five different groups of active sites were observed. It was thought worthwhile to study the chemisorption of hydrogen on a similar sample of Graphon, cleaned under the same experimental conditions, to see if the same active sites are involved in hydrogen chemisorption. Furthermore, since the activation energies for the chemisorption of hydrogen on carbon have been calculated theoretically [12], it is of interest to compare the theoretical values with values calculated from experimental kinetic data. This should also give support to the mechanism of chemisorption proposed in Parts I and II of this study.

The kinetics of hydrogen chemisorption have been studied at about 0.1 Torr starting pressure of the gas in the temperature range 80 to 600°C. Chemisorption rates have also been followed at 500°C at different starting pressures of hydrogen (0.020–0.50 Torr). At temperatures below about 80°C, the rate of chemisorption was so slow that it could not be measured accurately. At temperatures above about 600°C the reaction of hydrogen with carbon, resulting in the formation of methane, was measurable.

2. EXPERIMENTAL

(A) *Materials.* The carbon sample used was the well-known graphitized black, Graphon. It had been pre-oxidized to a weight loss of 18.6 per cent at 625°C in 0.5 Torr O₂ to introduce a significant active surface area, as previously discussed[13].

(B) *Apparatus and procedure.* The apparatus and procedure used have been described in detail[10, 11]. Briefly, the carbon sample (ca 0.1 g), held in a quartz boat, was outgassed at 1000°C for 10–12 hr to reduce the residual gas pressure to 10^{-8} Torr. After cooling to a desired temperature in vacuum, a known volume of H₂ was allowed to expand into the reactor. Adsorption was continuously

followed for times up to 1400 min, using a residual gas analyzer, a differential manometer, or a microadsorption balance where applicable. It is to be emphasized that in all runs, the maximum decrease in hydrogen pressure was < 5 per cent. This pressure change would produce a negligible change in adsorption rate during an adsorption run.

After the chemisorption of hydrogen in any one experiment, it was not possible to completely remove the hydrogen from the carbon surface by outgassing for 10–12 hr at 1000°C. That is, the residual gas pressure in the reactor at the end of this outgassing period was still significantly higher than 10^{-8} Torr. Since the rate of desorption of hydrogen is much slower than the desorption rate for oxygen [10, 11], a period of 60–72 hr at 1000°C was necessary to obtain a clean carbon surface. There is concern about degassing much above 1000°C because of possible annealing out of active carbon sites.

3. RESULTS

The amounts of hydrogen adsorbed at different starting pressures of hydrogen and at different temperatures, when plotted against time, gave curves which showed all the usual features of adsorption. The rate of adsorption was much faster in the beginning but fell off rapidly with time. The rate, however, increased with increasing pressure or temperature.

Several workers, in recent years have found the Elovich equation

$$\frac{dq}{dt} = a \exp(-\alpha q) \quad (1)$$

to be applicable to their adsorption data for a variety of systems. We have also used this equation to express our data on the chemisorption of oxygen on clean Graphon surfaces. We found that the equation is very well suited to explain the existence of different types of sites on the Graphon surface. We shall, therefore, be using the same

equation to present the data obtained in this investigation. The integrated form of equation (1) can be written as

$$q = \frac{1}{\alpha} \ln(1 + \alpha at) \quad (2)$$

where q is the amount adsorbed at time t and a and α are constants.

Elovich plots of the chemisorption data at different pressures and at different temperatures are shown in Figs. 1 and 2, respectively. The maximum amount of hydrogen chemisorbed was about 15×10^{18} atoms/g, or assuming the chemisorption of one H atom per edge carbon atom, the area occupied by the hydrogen would be about $1.3 \text{ m}^2/\text{g}$. This means that the maximum coverage of the Graphon surface with hydrogen was about 1.3 per cent. The more interesting features of these plots are as follows:

- (i) The plots show breaks, the number of breaks and the time of appearance of a break depending upon the adsorption pressure or the adsorption temperature. The slopes of these linear regions at each temperature and at each pressure were measured and indicate the existence of four different kinetic stages of adsorption.
- (ii) These different kinetic stages appear after the chemisorption of a definite amount of hydrogen, independent of adsorption temperature or pressure.
- (iii) The first kinetic stages are absent in higher temperature or higher pressure runs. The latter kinetic stages could not be observed in lower temperature or lower pressure runs. This is due to the fact that at lower temperatures or at lower pressures the rate of adsorption is slow and chemisorption on only the most active groups of sites could be observed in 1400 min. As the temperature or the pressure is increased, the rate of adsorption thereby increases; and, consequently, adsorption on less

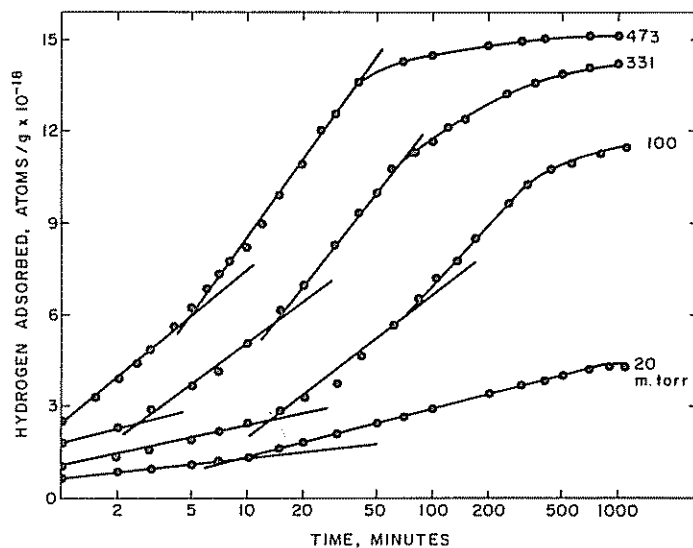


Fig. 1. Chemisorption of hydrogen on Graphon at 500°C and at different pressures. The Graphon was previously activated in O₂ to 18.6% weight loss.

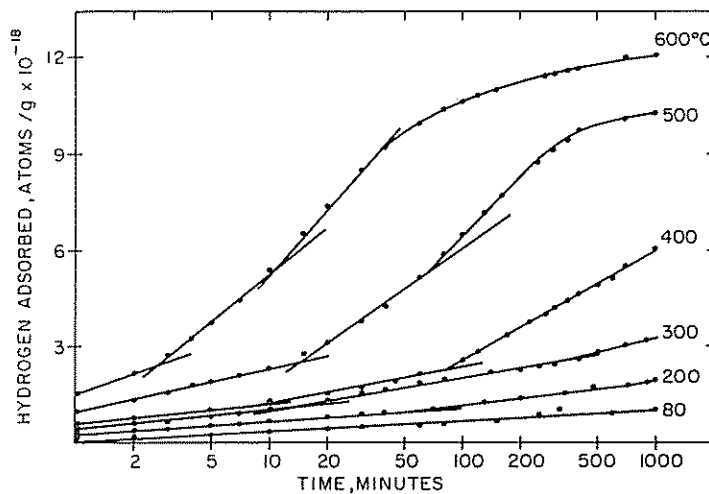


Fig. 2. Chemisorption of hydrogen on Graphon at 0-10 Torr pressure and at different temperatures. The Graphon was previously activated in O₂ to 18.6% weight loss.

active groups of sites could also be observed. However, at higher pressures or at higher temperatures the rate of adsorption was so fast that adsorption on the most active groups of sites was completed in the time period between the exposure of the sample to the gas and the first measurement.

In order to further verify that these q -log t plots do show linear regions and are not continuous curves, the slopes were calculated at each data point for the plots at 200, 300, 400, and 500°C at 0.1 Torr starting pressure of hydrogen. The plot of slope vs. the amount adsorbed at each point is shown in Fig. 3. All of the data points can be grouped into four different linear regions in slope, showing that the slope changes only in a discontinuous manner. A slight scatter in the points is expected, since slopes have been calculated with the data obtained at four different temperatures. Figure 4 presents additional strong evidence in favor of the

existence of breaks in the q -log t plots. It further supports strongly the concept of different kinetic stages, corresponding to adsorption on different types of active sites, as was previously proposed from our oxygen chemisorption results [11].

The rate parameters a and α of the Elovich equation were calculated for each adsorption region at all adsorption temperatures, using equation (2). These rate parameters are presented in Table 1. It is seen that both a and α are different for adsorption in different linear regions. However, for adsorption in any linear region, whereas α is almost independent of the adsorption temperature, a is strongly temperature dependent. This temperature dependency of a has been used to calculate the activation energy for adsorption in the different linear regions.

Arrhenius plots for the rates of adsorption on different types of sites are shown in Fig. 4. Activation energies calculated from these linear plots are also shown. It is seen that the

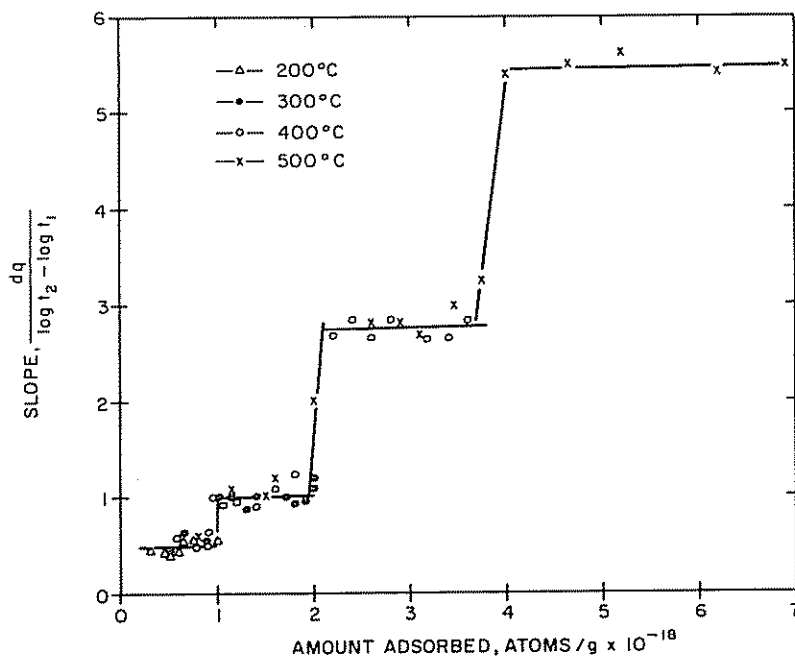


Fig. 3. Slopes of Elovich plots as a function of amount of hydrogen adsorption at 200, 300, 400 and 500°C. Hydrogen pressure, 0.10 Torr.

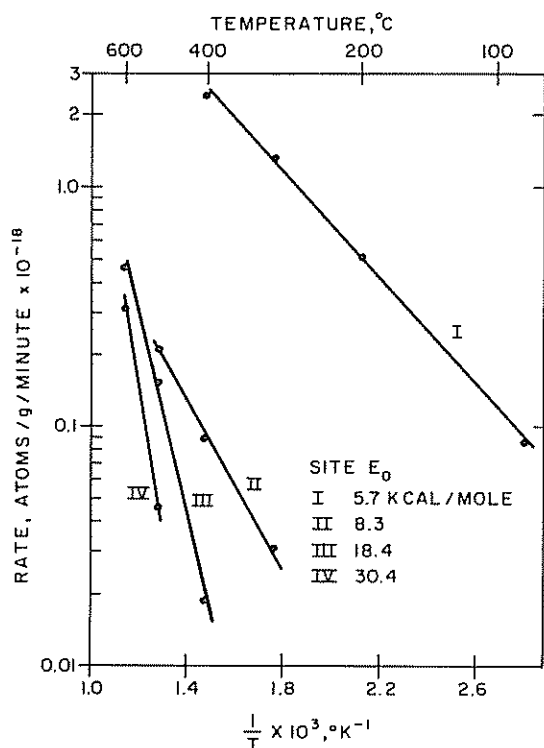


Fig. 4. Arrhenius plots of hydrogen chemisorption rates in the various stages of adsorption on Graphon. Hydrogen pressure, 0.10 Torr.

activation energy is different for adsorption on different groups of active sites. Similar plots were obtained when the rates were

plotted at different amounts of surface coverages in any one linear region. Activation energies calculated from these plots are, in turn, plotted against the amount of hydrogen chemisorbed in Fig. 5. It is interesting to note that the activation energy is almost independent of surface coverage for adsorption in any one linear region but is different for adsorption in different linear regions. This further supports the concept that there are discrete types of sites on the Graphon surface associated with different activation energies.

The fact that the activation energy is independent of surface coverage for adsorption on any one group of active sites is a direct result of the experimental observation that α is independent of the adsorption temperature. Although this is not a common occurrence, it has been found to be so in several cases [11, 14, 15].

4. DISCUSSION

The existence of active sites on carbon surfaces has been suggested by several workers. Rideal and Wright [16], while studying the oxidation of carbon, suggested that there are three types of surfaces on carbon which behave differently in oxidation reactions. Long and Sykes [17] considered that the same charcoal contained two different types of sites, one of which participates

Table 1. Parameters in the Elovich equation for adsorption of hydrogen on Graphon at different temperatures and stages

Temp. (°C)	Stage							
	I		II		III		IV	
	α^*	a^\dagger	α	a	α	a	α	a
80	6.1	0.09	—	—	—	—	—	—
200	5.1	0.51	—	—	—	—	—	—
300	5.3	1.32	2.56	0.03	—	—	—	—
400	4.9	2.42	2.42	0.06	0.72	0.02	—	—
500	—	—	2.56	0.21	0.74	0.16	0.45	0.05
600	—	—	—	—	0.72	0.46	0.40	0.31

*atoms⁻¹ g $\times 10^{18}$.

†atoms g⁻¹ min⁻¹ $\times 10^{-18}$.

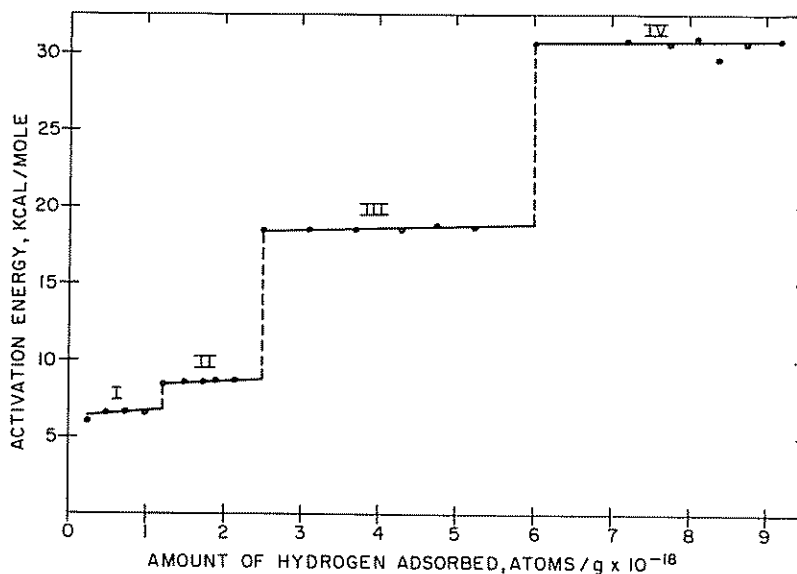


Fig. 5. Change of activation energy for hydrogen chemisorption on Graphon with amount adsorbed.

in reactions with steam and the other in reactions with carbon dioxide.

Taylor and co-workers[15, 18], in their studies on the chemisorption of gases on a wide variety of solid surfaces, found their Elovich plots to have breaks and abrupt changes in slope. They attributed this behavior to adsorption on different types of sites.

Walker and co-workers[19, 20], while studying the chemisorption of oxygen at temperatures between 100–575°C, observed that the chemisorption involved more than one type of site. We previously studied the chemisorption of oxygen on Graphon in the temperature range –78 to 160°C and in the pressure range 7×10^{-6} – 7.6×10^2 Torr[10, 11] and concluded that chemisorption took place on five different types of sites.

However, in the present study of hydrogen chemisorption on a similar sample of Graphon, chemisorption on only four types of sites has been observed. This may be attributed to the fact that the rate of chemisorption of hydrogen is much slower than the rate of chemisorption of oxygen.

Therefore, the fifth group of active sites could be observed only if the chemisorption experiments were carried out at higher temperatures. This possibility was examined by performing one experiment at 700°C. However, it was found that the carbon-hydrogen reaction, resulting in the formation of methane, was sufficiently rapid at this temperature so as to make measurements of chemisorption rates difficult. Furthermore, since the gasification of the carbon sample in hydrogen could result in surface alteration, additional experiments at higher temperatures were not conducted.

Puri and co-workers[21, 22], in their experiments on the chlorination of sugar and coconut charcoals in the temperature range 30–1200°C, observed that hydrogen from charcoals is eliminated in steps. This they attributed to the bonding of hydrogen with different energy levels.

The existence of these different types of sites can be attributed to differences in the geometric arrangement of the surface carbon atoms. As the graphite surface presents several carbon-carbon distances to the

Table 2. Comparison of experimental and theoretical values of activation energy for chemisorption of hydrogen on graphite

Site	Experimental		Theoretical [12]	
	<i>E</i> , kcal/mole	C-C distance, Å	C-C distance, Å	<i>E</i> , kcal/mole
I	5.7	3.62	3.62	9
II	8.3	3.35	3.35	11
III	18.4	2.84	2.84	19
IV	30.4	2.46	2.46	28
V	—	1.42	1.42	50

incoming hydrogen molecule, the activated complex formed between H₂ and two surface carbon atoms would be expected to have different potential energy configurations dependent upon these spacings between the carbon atoms. Thus, the activation energy for the dissociative chemisorption of hydrogen would be expected to vary. Sherman and Eyring [12] made theoretical calculations of the energy of activation for the dissociative chemisorption of hydrogen on a carbon surface and found the values to vary with the carbon-carbon spacings. Table 2 presents a comparison of these theoretical values of activation energy with our experimental values. The carbon-carbon distances selected in Table 2 are those which a hydrogen molecule would be most likely to encounter when approaching closely to the carbon surface. The spacing of 2.46 Å is for the configuration of carbon atoms terminating the {10 $\bar{1}$ 1} face; the spacings of 1.42 and 2.84 Å, for terminating the {11 $\bar{2}$ 1} face; and the spacings of 3.35 and 3.62 Å, for distances between edge carbon atoms in adjacent basal planes. Agreement between the experimental and theoretical values is reasonably good, thus supporting the concept presented in this paper and Parts I and II of this study that these carbon-carbon spacings act like discrete types of sites on which the chemisorption of gases, in general, can take place.

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