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Kinetics of Chemisorption of CO_2 on Scandia: A New Rate Equation

J. A. PAJARES, J. L. GARCÍA FIERRO, AND S. W. WELLER[1]

Instituto de Catálisis y Petroleoquímica del C.S.I.C., Serrano, 119, Madrid (6), Spain

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The kinetics of chemisorption of CO_2 on Sc_2O_3 has been studied, in the ranges of 1–20 Torr and 20–300°C, by using a gravimetric method. Experimental results on the effects of pressure, temperature, and the state of hydroxylation of the surface have been obtained. Above 1.5 Torr, the rate of adsorption depends linearly on the pressure of CO_2; the state of the surface has a strong influence on the amount of chemisorbed CO_2 and on the rate of adsorption, both higher as the number of hydroxyls in the surface becomes lower. The data fit well an integrated kinetic law,

$$\ln [q_e/(q_e - q)] = kPt,$$

based on a Langmuirian treatment. The quantity q_e is the adsorbed amount in the equilibrium isotherm, and the fraction of clean surface is given by $(q_e - q)$, which is an experimentally measurable quantity. In plots of the integrated equation, $\log [q_e/(q_e - q)]$ vs t, the intercepts give information about q_0, the quantity chemisorbed very rapidly at "zero time." The value of q_0 is related to the gas pressure and to the state of surface dehydroxylation.

INTRODUCTION

Reliable data on adsorption kinetics are very important in the study of catalytic processes: Rates of adsorption can be used to support or to reject the intervention of adsorption as a rate-determining step; the possible existence of an activation energy of adsorption is of interest in interpreting catalytic processes; and knowledge of a kinetic law valid over a wide range of pressures and temperatures is an ultimate goal in kinetic studies.

The Elovich equation,

$$dq/dt = ae^{-\alpha \cdot q}, \tag{1}$$

has been widely used in interpreting kinetic results in different gas/solid systems. Its use and analysis has been well studied in two excellent reviews (*1*, *2*). Good examples of its application in simple systems of reversible chemisorption are found in the work of Shelef and co-workers (*3*). However, Eq. (1) fits fairly well kinetic data related to more complex systems, such as irreversible chemisorption with formation of a superficial compound, the growth of an oxide layer in metal corrosion, etc., characteristic of a process or a group of processes of an activated character; for this reason its mechanistic implications have little or no relevance.

Empirical power equations have been preferred by some authors (*4*). References to their use in different gas/solid systems are given in (*1*). However, their application has been very restricted, and their generalizations have not had much success.

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[1] Visiting Professor from the Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, N. Y. 14214.

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Some mathematical expressions derived from the kinetic treatment of Langmuir (5) have more theoretical support. This author envisages the rate of removal of the gaseous phase as the difference between the rates of adsorption and desorption:

$$dq/dt = k_a P(1 - \theta) - k_d \theta \qquad (2)$$

For small coverages, the second term in the r.h.s. is practically zero, so that the expression

$$dq/dt = k_a P(1 - \theta) \qquad (3)$$

gives the adsorption rate. Some modifications, mainly in relation to the clean surface factor, $(1 - \theta)$, have been made by different authors and are discussed in (*1*). The introduction of a precursor has been recently discussed by Weinberg *et al.* (*6*).

The Langmuir equation supposes that the number of adsorption sites is constant over an unrestricted range of temperatures. This statement is seldom confirmed by experimental results. Usually the systems obey a pseudo-Langmuirian law, the adsorbed monolayer becoming progressively smaller at higher temperatures. This lack of coherence was emphasized some time ago by Dushman. (*7*)

In this work, the kinetics of chemisorption of carbon dioxide on scandium oxide was studied, while taking account of the effects of pressure, temperature, and state of the surface of the adsorbent; the experimental data were treated according to a kinetic law that fits this system. This law is based on the mathematical treatment of Langmuir, but the clean surface factor is given by $(q_e - q)$, the difference between the amount of CO_2 adsorbed at equilibrium, q_e, taken from the experimental adsorption isotherm, and the amount adsorbed at a time t, q.

TABLE 1

Sc_2O_3 Characterization

	Starting material	Treated at 700°C
Impurities	Y_2O_3, Yb_2O_3 (0.03%) Bi, Pb, Si (traces)	—
RX	Crystalline	—
S_{BET} ($m^2\ g^{-1}$)	16.8	16.0
V_{pore} ($cm^3\ g^{-1}$)	—	0.06
Pore radius (Å)	—	$\simeq 75$
$DTA_{25-1050°C}$	No thermal peaks	—
$TGA_{10°C\ min^{-1}}$	−0.16% wt	—

Data on the energetics of adsorption of CO_2 on Sc_2O_3 have been previously published (*8–10*). The isotherms fit the Freundlich equation and relatively high coverages were reached; their shapes belong to type I of the BDDT classification, the flat part corresponding to coverages progressively smaller with higher temperatures. The isobar presents a shoulder around 200°C, typical of a chemisorption process. The ir spectra show the existence of two adsorbed species, a symmetric and a bidentate superficial carbonate. The heat of adsorption falls exponentially with coverage from a value $Q = 25.3$ kcal mol^{-1} for $\theta = 0.12$ to $Q = 9.5$ kcal mol^{-1} for $\theta = 0.37$. Differential molar entropies of adsorption at 250°C are characteristic of a mobil superficial species, such as that found for the system CO_2/γ-alumina by Rosynek (*11*).

Low (*1*) has emphasized the lack of data required for a sound knowledge of the effect of pressure on the rate of adsorption. In his review, as in more recent work (*2*, *12*), experimental data are fitted to the Elovich equation, the study being reduced to the investigation of the effect of pressure on the parameters α and a. The effect of the state of the surface has been, in general terms, studied very little.

EXPERIMENTAL

Materials. Sc_2O_3 (99.9 wt% pure) was supplied by Fluka. In Table 1 a summary of the structural and textural characteristics of the starting powder as well as after a thermal treatment at 700°C in air

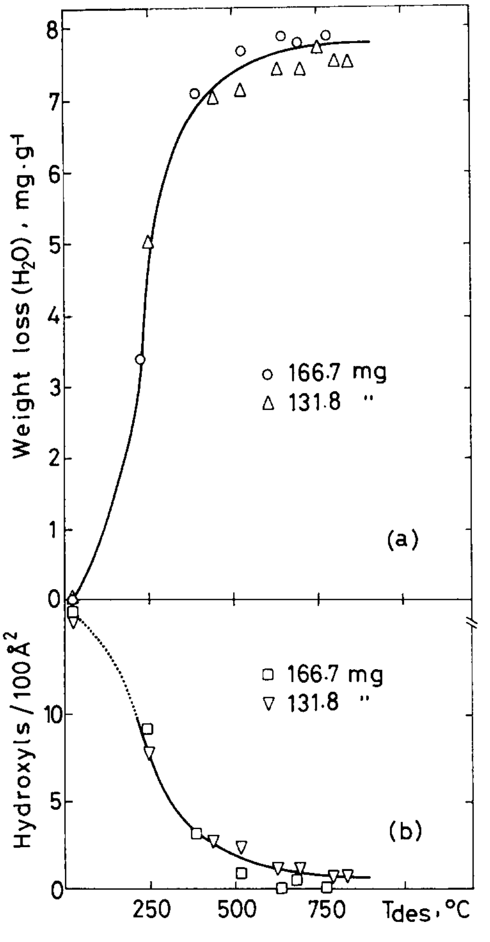

FIG. 1. (a) Weight loss (H_2O) for two Sc_2O_3 samples, with variable equilibrium temperatures and equilibrium values. (1b), Remaining number of OH/100 Å². Sample pumped at 830°C as reference.

for 4 hr, as used in this study, is given. Details have been given elsewhere (*9*, *13*). Nitrogen adsorption isotherms show a de Boer A type hysteresis, typical of regular cylindric pores, open by both ends, or of a bottle model with short, wide necks. Their nature is changed little by thermal treatment, although the pore radius of the material heated at 700°C diminishes slightly through generation of mesopores at the expense of original macropores (*14*).

The ir spectra of surface hydroxyls, with a clear band at 3665 cm⁻¹, have been studied previously (*9*). The weight loss (H_2O) for two samples with different weights, treated at rising temperatures of degasification, are given in Fig. 1a. Data correspond to the equilibrium, the samples heated at 830°C being taken as reference. In Fig. 1b these results are given as number of OH per 100 Å²; above a pumping temperature of 550°C, less than 1 OH/100 Å² remains in the surface.

CO_2, 99.998% pure, was obtained from Societé de L'Air Liquide. Before storage in the apparatus it was passed through a purification train and repeatedly condensed at liquid nitrogen temperature, only the middle fraction being taken. Helium, 99.995% pure, from Sociedad Española del Oxígeno, for calibrations and corrections, was used.

Apparatus and experimental procedure. Measurements were carried out by means of a Cahn RG electrobalance connected to a conventional high-vacuum and gas-handling system. The Sc_2O_3 sample was placed in a small cylindrical basket made of quartz, 12 mm in diameter, 9 mm long, with a ring of nichrome wire, 0.05 mm in diameter. To eliminate sample losses the basket was covered by a fine, perforated aluminum sheet, through which gases can easily pass. Hanging wires 50 cm long and about 30 mg in weight were used. Sidearm tubes 50 cm long and 22 mm in i.d., with small pieces of tubing at the bottom to bring the thermocouples near the sample and counterweight as much as possible, were coupled through ground male-female conical joints. Two coaxial tubular furnaces for heating purposes were employed. Care was taken to make the whole gravimetric set-up a symmetrical unity to suppress problems due to gaseous convection streams. The dead volume was about 4 liters.

Experiments on Sc_2O_3 samples between 300–600 mg in weight were carried out; a study on fine powdered samples ($d < 0.053$ mm) of 100–600 mg in weight and on weakly pressed pellets broken into small grains had been performed previously; adsorbed quantities and initial rates proportional to the sample weight were obtained in all cases. Therefore, the last type of sample was preferred due to its easiest handling.

Throughout the series of runs for studying the effect of pressure and temperature, the sample was always pumped out at 10^{-6} Torr and 550°C for 24 hr. The experiments were carried out at a practically constant pressure because of the relatively large dead volume of the adsorption unit.

At low pressures, below 1 Torr, the thermomolecular effect was noticed. At high pressures, gas convection streams determine a drawing phenomenon, very acute above 100 Torr and difficult to eliminate due to the imperfect symmetry of the system. The effects of gas pressure and the expansion against a vacuum produce a wave motion along the balance arms causing a gravimetric signal with an important peak-to-peak wideness for the first of these factors, and a small peak-to-peak band for the second when the gas pressure is low or moderate. In any case, a level corresponding to the middle of the peak was taken as final reading.

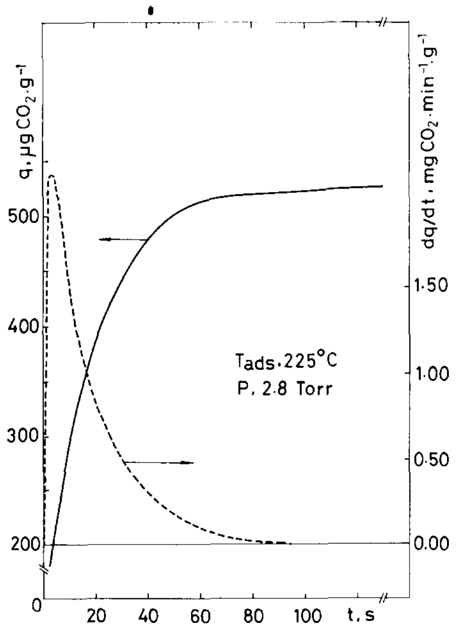

FIG. 2. Kinetic run. —, CO_2 adsorbed, integral data; – – –, adsorption rates.

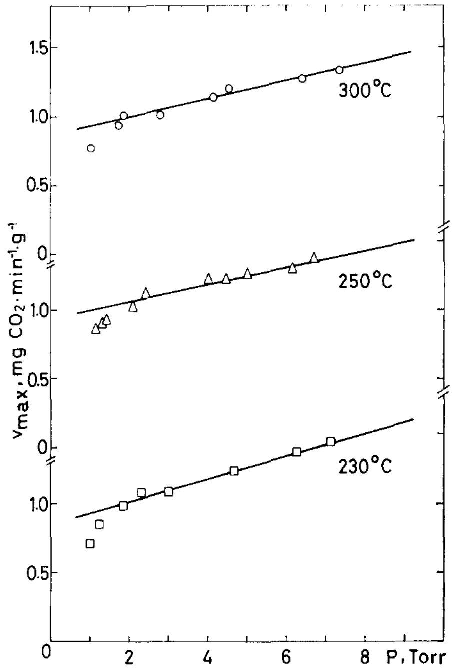

FIG. 3. Effect of pressure on initial adsorption rates.

Integral data of the quantity of adsorbed CO_2 and differential data on rates of adsorption determined by means of a derivator system were registered simultaneously, a high recorder speed being maintained for a better measuring resolution. Recording of differential data presents problems, introduced by the filtering system, that modifies the response time of the apparatus, so that initial rates appear with a delay of some seconds in the most unfavorable cases. Different filtering positions introduce different delay times, calling for different calibrations; a general method of correction of this effect is difficult to unify. For this reason, in the mathematical analysis integral data were preferred, the differential ones being used mainly to calculate the initial rates and for comparison with those obtained from the integral results.

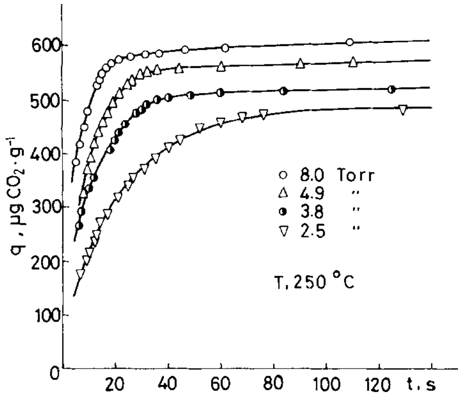

FIG. 4. Integral results at 250°C and different pressures.

An example of an experiment is given in Fig. 2. The kinetics were measured at 225°C and 2.8 Torr, the recorder speed being 60 mm min^{-1}. The adsorbed quantity, q, increases quickly reaching the equilibrium value in a time a little longer than a minute. The initial rate of adsorption, dq/dt, reaches a maximum value after 3 sec, coming down quickly; after 1 min its value becomes very small, and its determination is inaccurate. The reading corresponding to the maximum value, denoted as v_{max} in Figs. 3 and 5, was taken as the initial rate of adsorption.

The elimination of the heat evolved in the CO_2 adsorption on Sc_2O_3, $Q < 10$ kcal mol^{-1} for coverages above $\theta = 0.15$, is not a particularly important problem for this system.

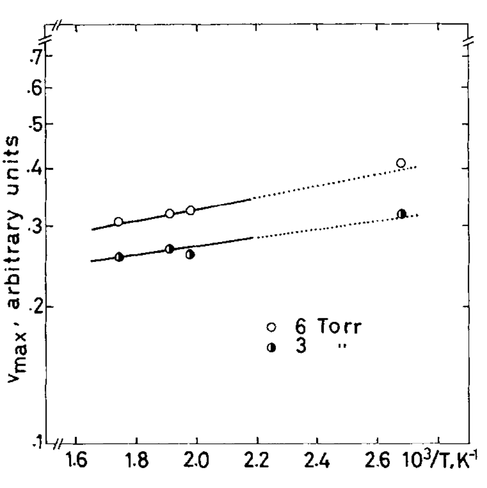

FIG. 5. Arrhenius plot of initial adsorption rates at pressures of 3 and 6 Torr.

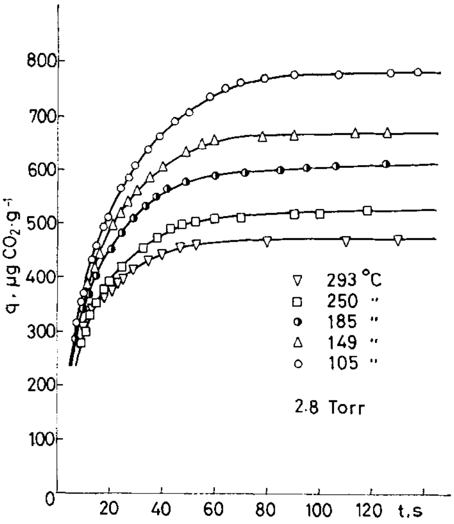

FIG. 6. Integral results at 2.8 Torr and different temperatures.

EXPERIMENTAL RESULTS

Effect of pressure. The study of the effect of pressure on the highest recorded rate of adsorption, v_{max}, has been limited to a restricted range, 1–20 Torr, where problems introduced by gas dynamics are reduced to a minimum. From this viewpoint, the data of Shelef *et al.* (*3*) on adsorption rates at a pressure of 3 Torr are a good example of a choice of particularly favorable experimental conditions.

In Fig. 3 results on the effect of pressure at three temperatures, 230, 250, and 300°C, are given. Above 1.5 Torr the adsorption rate shows a linear dependence of the pressure. Extrapolation to zero pressure would determine a significant initial rate of adsorption, since the straight lines do not cross the ordinate axis at the zero point. At pressures below 1.5 Torr, the plot dq/dt vs P bends toward the origin. Mathematical analysis is complicated since account must be taken of the intervention of the thermomolecular effect and of the limitations in the mass transport to the gas/solid interphase.

In Fig. 4 adsorbed weights of CO_2 on a sample of Sc_2O_3 at 250°C, starting with different CO_2 pressures (8.0, 4.9, 3.8, and 2.5 Torr), are given. The adsorbed quantities for the largest times are equal to the data obtained from the equilibrium adsorption isotherm (*9*, *10*).

Effect of temperature. In Fig. 5 initial rates of adsorption vs $10^3/T$, obtained at constant pressures, 6 and 3 Torr, in the range of 100–300°C, are given. Calculations of the temperature coefficient gave negative values, -1.1 and -0.7 kcal mol^{-1}, respectively. These results are typical of either a non- or slightly activated system, the shape of the isobar itself suggesting a small activation energy.

In Fig. 6 data for the adsorption of CO_2 on Sc_2O_3 at a constant pressure of 2.8 Torr, in the range of 105–293°C, are given. The final adsorbed quantities correspond to those drawn from the adsorption equilibrium isotherms, the straight parts of the plots being reached in shorter times at higher temperatures.

Effect of the state of hydroxylation of the surface. From ir spectra it is inferred that CO_2 does not interact with surface hydroxyls, at least when the hydroxyl population is low or moderate. However, both chemical species are competitive on the surface as can be seen in Fig. 7 where equilibrium quantities of CO_2 adsorbed at 23°C, denoted as q'_e, have been plotted against the degasification temperature; the results were taken from a series of kinetic experiments made at a constant pressure, 3.2 Torr, on a sample that was previously hydroxylated by treatment with water vapor. Similar results have been obtained for CO_2 adsorption on ZnO by Morimoto and Morishige (*15*).

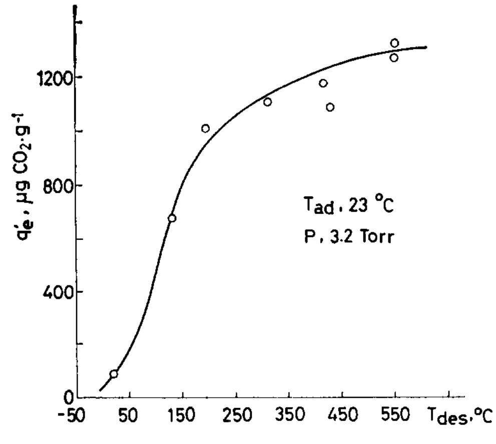

FIG. 7. CO_2, adsorbed at 23°C at equilibrium, versus pumping temperature.

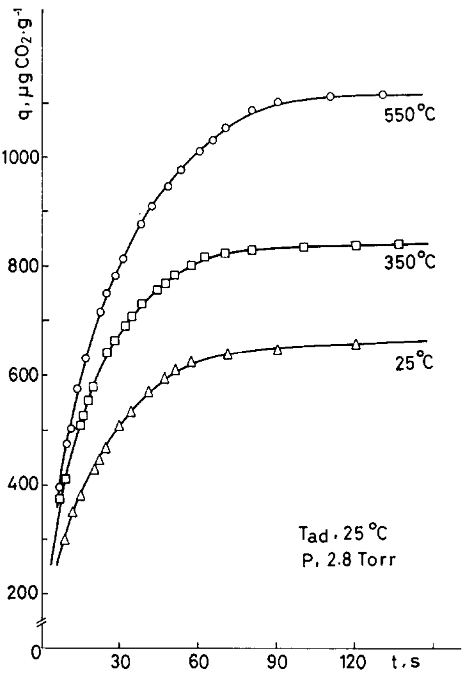

FIG. 8. Kinetic runs: integral results, at 25°C and 2.8 Torr, on a Sc_2O_3 sample dehydroxylated at three different temperatures (25, 350, and 550°C).

The surface population of CO_2 at 23°C, calculated from the equilibrium isotherm, at a $P_{CO_2} = 100$ Torr, on the sample degasified for 24 hr at 550°C, gives a surface coverage of $\theta = 0.46$, equivalent to scarcely three CO_2 molecules per 100 Å^2. Comparison with Fig. 1b shows that the number of adsorbed CO_2 molecules is greater when the number of superficial hydroxyls becomes lower, the Sc_2O_3 surface introducing restrictions to a higher coverage for chemisorbed CO_2 at this temperature.

The influence of the state of hydroxylation of the Sc_2O_3 surface on the kinetics of chemisorption can be seen in Fig. 8, where integral data at 25°C and 2.8 Torr, obtained on a Sc_2O_3 sample previously pumped out at 25, 350, and 550°C for 8 hr, are given. The degree of OH coverage for the surface of scandia was around a total of 4 and 1 OH/100 Å^2, respectively, for these previous degasification treatments.

DISCUSSION

The Elovich law was the first kinetic model tested. An example of a tentative fitting of experimental data is given in Fig. 9 (curve of full circles). Obviously, this kinetic law is not obeyed.

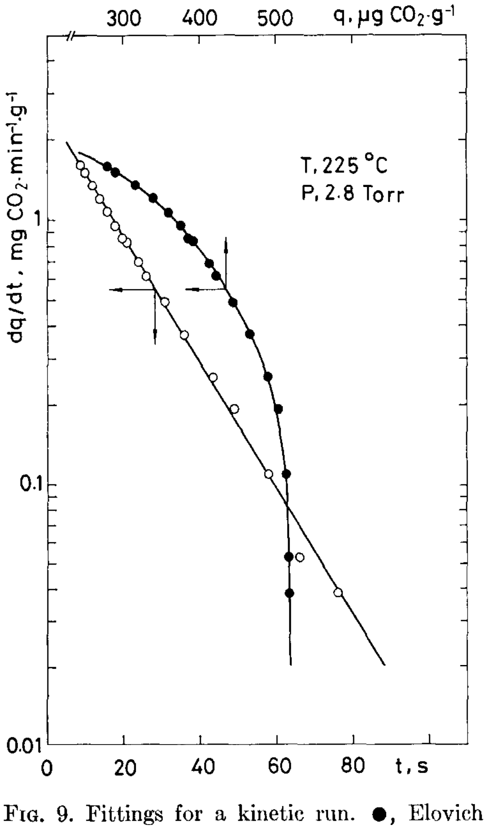

Fig. 9. Fittings for a kinetic run. ●, Elovich; O, Eq. (5) in the form $dq/dt = kPe^{-kPt}$.

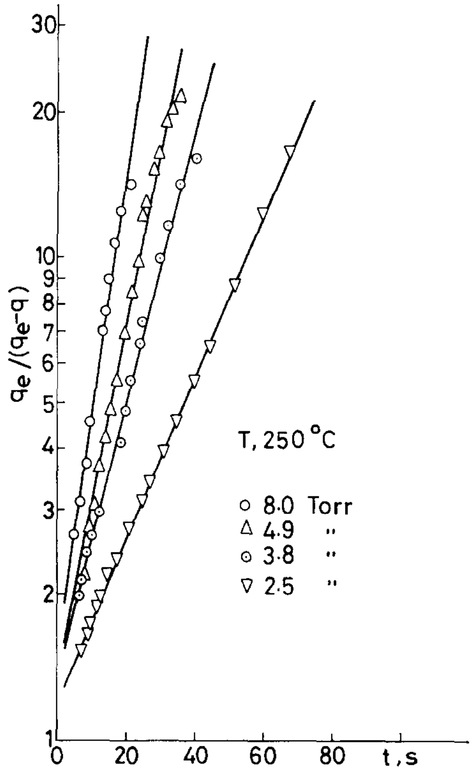

Fig. 10. Kinetic fittings for integral data at 250°C.

When the experimental results are plotted according to the expression:

$$dq/dt = kP(q_e - q), \qquad (4)$$

fairly good fits are obtained, the rate of adsorption being a function of pressure and of $(q_e - q)$; q_e, constant at a defined temperature and pressure, is the amount of CO_2 adsorbed at equilibrium (taken from the equilibrium isotherm), and q is the weight of CO_2 adsorbed at time t. The equation, first order, is the same as that used by Langmuir, with an important change: the substitution of the clean surface factor $(1 - \theta)$, proportional to the number of adsorption centers in the Langmuirian treatment, by the measurable quantity $(q_e - q)$. The quantity q_e is not constant with temperature, but it follows the course of the adsorption isobar,

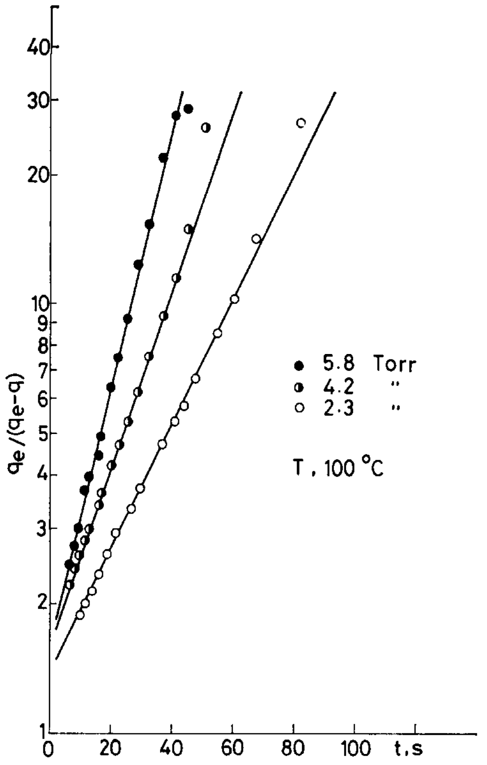

FIG. 11. Kinetic fittings for integral data at 100°C.

becoming progressively smaller at higher temperatures.[2]

By integration of Eq. (4), the expression

$$\ln[q_e/q_e - q)] = kPt \qquad (5)$$

is obtained. Fittings for both differential and integral data corroborate the applicability of Eqs. (4) and (5). In Figs. 10 and 11 fittings of results at different pressures, at 250 and 100°C, are given. By extrapolation at zero time, values of $q_e/(q_e - q)$ higher than 1, which is the value that theoretically corresponds for an initial adsorption $q = 0$, are obtained. From these points, q_0, the amount of CO_2 adsorbed in an infinitesimal time after the start of adsorption, can be calculated. A summary of the deduced parameters is given in Table 2.

TABLE 2

Effect of Pressure: Parameters from Fittings to the Equation $\ln[q_e/(q_e - q)] = kPt$

T (°C)	P (Torr)	$k\cdot 10^2$ (Torr^{-1} sec^{-1})	$q_e - q_0$ (μg of $CO_2\,g^{-1}$)	q_0 (μg of $CO_2\,g^{-1}$)
250	8.0	1.39	404	214
250	4.9	1.72	454	127
250	3.8	1.67	391	148
250	2.5	1.53	420	84
100	5.8	1.23	725	370
100	4.2	1.15	621	354
100	2.3	1.54	639	185

In Fig. 12 fittings of integral data obtained at adsorption temperatures in the range of 105–305°C and 2.8 Torr are shown. In Table 3 some additional results

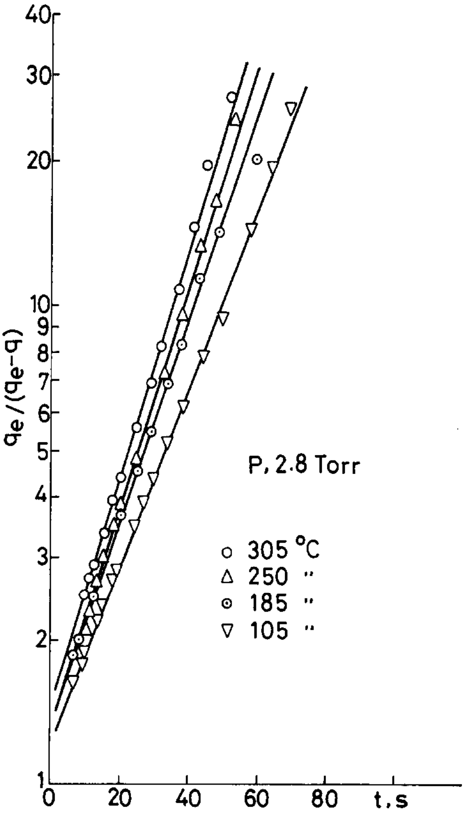

FIG. 12. Kinetic fittings at 2.8 Torr and 105–305°C.

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[2] In fact, the plot of Fig. 9 (open circles) comes from Eq. (5) in the form $q = q_e - q_e\cdot e^{-kPt}$. By differentiation and taking logarithms, the expression $\ln dq/dt = -kPt + \ln kPq_e$ is obtained, useful for comparison purposes with the Elovich plot.

TABLE 3

Effect of Adsorption Temperature: Parameters from Fittings to the Equation $\ln[q_e/(q_e - q)] = kPt^a$

T (°C)	$k \cdot 10^2$ ($Torr^{-1}$ sec^{-1})	$q_e - q_0$ (μg of $CO_2\,g^{-1}$)	q_0 (μg of $CO_2\,g^{-1}$)
105	1.40	621	174
185	1.64	437	188
225	1.69	392	145
250	1.87	405	125
293	1.72	301	187
305	2.01	332	136

[a] $P = 2.8$ Torr.

are given. The temperature coefficient of k is very small, corresponding to an activation energy of ca. 0.8 kcal mol^{-1}. The values of q_0 are remarkably constant for constant pretreatment temperature (550°C) and adsorption pressure.

Analysis of results obtained on samples of Sc_2O_3 with different degrees of surface hydroxylation are given in Fig. 13, where the results of experiments carried out at 25°C and 4.6 Torr on a sample evacuated at 21, 185, 350, and 525°C, are fitted according to Eq. [5]. Values for $(q_e - q_0)$ and adsorption constants are given in Table 4.

The sample behavior depends strongly on the outgassing temperature. When the sample is well hydroxylated, by degasification at low temperatures, good fits to Eq. (5) were not found; adsorption constants are low and values for $(q_e - q_0)$ are very small. Perhaps it would be interesting to investigate in detail what the adsorption reaction is at these temperatures and hydroxylation degrees, because it will not be rare to find a change in the mechanism of adsorption with the formation of a surface bicarbonate such as that found in the system CO_2/γ-alumina by Rosynek (*11*).

TABLE 4

Effect of the State of Hydroxylation of the Surface: Parameters from Fittings to the Equation $\ln[q_e/q_e - q)] = kPt^a$

T_{degas} (°C)	$k \cdot 10^2$ ($Torr^{-1}$ sec^{-1})	$q_e - q_0$ (μg of $CO_2\,g^{-1}$)	q_0 (μg of $CO_2\,g^{-1}$)	OH/100 Å^2
21	0.61	164	531	Total
185	0.57	220	583	12
350	1.41	643	232	4
525	1.37	936	204	1.5

[a] $T = 25$°C; $P = 4.6$ Torr.

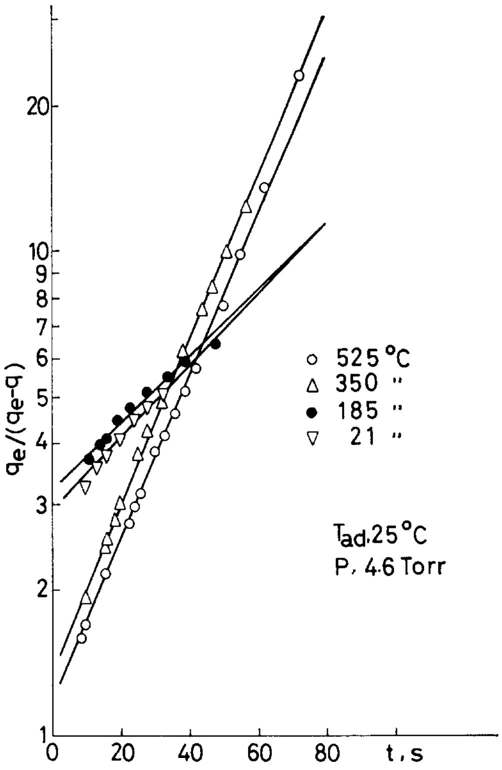

FIG. 13. Kinetic fittings at 25°C and 4.6 Torr, for a sample dehydroxylated at four different temperatures (21, 185, 350, and 525°C).

If the Sc_2O_3 sample underwent a stronger pumping treatment, good kinetic fittings are found, with large $(q_e - q_0)$ values, which reflect the degree of surface dehydroxylation. The calculated q_0 for samples pumped out at 350 and 525°C have equal values.

The fundamental point of Eq. (4) is the introduction of a driving force, $(q_e - q)$, as the factor related to the clean surface fraction. The factor $(q_e - q)$ is obviously proportional to the available fraction of adsorption centers, and it can be experimentally measured. This method eliminates indeterminate variables in the calculations of such a factor, such as, for instance, those related to the use of the BET monolayer or the value deduced from the Freundlich isotherms cross-point when both do not reach the same values; or those associated with the determination of a specific area for the adsorbed molecule of gas; or those derived from numerous systems with a pseudo-Langmuirian behavior, the isotherms fitting a Langmuir equation at each temperature, but the value for the monolayer progressively falling at increasing temperatures.

The intercepts of the $\ln[q_e/(q_e - q)]$ vs time plots allow the calculation of q_0, the amount of CO_2 initially adsorbed at "zero time." As Table 2 shows, at constant temperature the q_0 values increase with increasing pressure. This may be a kinetic factor related to the frequency of collisions per unit area. At constant pressure there is no clear dependence of q_0 with adsorption temperature. In any case, Eq. (5) permits the *experimental* determination of a quantity, q_0, corresponding to a very quick process. This is an improvement over the trial and error determination of the correction factor, needed to fit data to the Elovich law in a good deal of gas/solid systems (*1*, *2*, *12*, *16*).

The magnitude of the $(q_e - q_0)$ value at a constant pressure depends mainly on the change of q_e with temperature. As Table 3 illustrates, this effect is greatest at low temperatures; e.g., $(q_e - q_0)$ is very high: 621 $\mu g\ g^{-1}$, at 105°C; 936 $\mu g\ g^{-1}$, at 25°C (Table 4). By contrast, at constant temperature, $(q_e - q_0)$ hardly changes with pressure (cf. Table 2).

The influence on the $(q_e - q_0)$ value of the dehydroxylation state of the surface is very important. Data are collected in Table 4. The $(q_e - q)$ values are clearly associated with the extent of surface dehydroxylation, given in the last column of the table.

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