NOTES

The Freundlich Model of Adsorption for Calculation of Specific Surface Areas

INTRODUCTION

The specific surface area of solids and the surface area occupied by the active phase (metal or oxide) on a support are parameters of the utmost importance in adsorption and catalysis. For the determination of the former, the BET equation is universally established. For the evaluation of the latter the works of selective chemisorption, initiated by Emmett and Brunauer (1), for metals and by Bridges et al. (2) and Weller et al. (3), for oxides have come to represent important contributions. Some of the classical models of adsorption have also been used for evaluation of specific surfaces (Langmuir equation) (4) and the dispersion of supported metals or oxides (Freundlich equation) (5). Both of them are applicable to physisorption as well as chemisorption processes.

Although the Freundlich equation is not more theoretically justified than the Langmuir equation (the basic concept of localized, monolayer adsorption is assumed for both) the former is more widely obeyed. According to the statistical derivation, and assuming that the adsorption sites are distributed exponentially with respect to the energy of adsorption, the Freundlich equation becomes:

$$\lg C_A = \lg C_M + \frac{RT}{q_m} \lg a_0 + \frac{RT}{q_m} \lg P. \quad (1)$$

C_A is the adsorption at pressure P; q_m has the physical meaning of a heat of adsorption at coverage $\Theta = 0.37$; a_0 is a constant. This equation requires that a family of isotherms at different temperatures cross at a common point at a pressure $P = 1/a_0$,

where the monolayer coverage is reached. The application of the Clausius–Clapeyron equation to (1) leads to an expression in which the heat of adsorption decreases exponentially with coverage.

Rudnitsky and Alexeyev (6) have recently elaborated equations for adsorption isotherms on adsorbents with heterogeneous surface, assuming the same exponential distribution for adsorption sites mentioned before. Those authors found that at high equilibrium pressures, the theoretical isotherms, $\lg \Theta$ vs $\lg P$ bend toward the pressure axis. In any case, the simpler Freundlich equation (1) for which the $\lg C_A$ vs $\lg P$ plots are straight lines, accounts fairly well for the physical behavior of the adsorption systems studied here.

Otto et al. (5) have extensively used Eq. (1) for the study of supported metals (Pt) and oxides (Cr_2O_3, Fe_2O_3, NiO, CuO). These authors found that NO adsorption at monolayer coverage, as calculated by extrapolation of the linear $\lg C_A$ vs $\lg P$ plots, is equal to the number of surface metal atoms calculated from crystallographic data (nonsupported catalysts) or by chemical analysis (supported catalysts at concentrations below 1%, where all the active phase is supposed to be on the surface). By assuming that the adsorption for supported metals or oxides at higher concentrations is similar to that on nonsupported catalysts, the fraction of the support surface occupied by the active phase can be calculated.

In this work, experimental data of CO_2 adsorption on the perovskite-type oxide $LaFeO_3$ are given. Equilibrium data of adsorption of N_2O (7), N_2 (8), CO (9), O_2 (10), and CO_2 (11) on oxides, obtained

previously in this laboratory, are also analyzed. These results provide new information on the applicability of the Freundlich equation for the evaluation of the adsorption monolayer and of specific surface areas.

EXPERIMENTAL

The $LaFeO_3$ sample was obtained by amorphous precursor decomposition as described by Delmon *et al.* (*12*). Briefly, a concentrated solution of metal nitrates and citric acid was evaporated at 343 K. The precipitated amorphous precursor was decomposed by heating at 923 K for 4 hr in air atmosphere. After this treatment a single perovskite phase was obtained as verified by thermogravimetric analysis and X-ray diffraction. The cylindrical pellets prepared by pressing the resultant powder at moderate pressure (2×10^6 N m^{-2}) were gently crushed in an agate mortar and particle sizes between 0.8 and 1.2 mm were taken for use. A more detailed account of the preparation method and also of the textural properties of perovskites obtained by this procedure can be found elsewhere (*13*).

The adsorption measurements were carried out in a conventional volumetric Pyrex glass high-vacuum system with a calibrated Schaevitz P-502-0004 pressure transducer. Temperatures were kept within ±0.5 K. Between successive experiments, the sample (2 g) was outgassed by means of a thermal treatment at 1.3×10^{-4} N m^{-2} and 773 K for 15 hr.

RESULTS AND DISCUSSION

In Fig. 1, equilibrium data, lg C_A *vs* lg P, of adsorption of CO_2 on the perovskite-type oxide $LaFeO_3$ at 432, 480, and 531 K are given. As it can be observed, the Freundlich equation is obeyed. The crossing point of the straight lines, as calculated by the least-square method, yields an adsorption for the monolayer of 8.6×10^{18} molec m^{-2} corresponding to a pressure of 3.4×10^4 atm (1 atm = 1.01×10^5 N m^{-2}). In this case the lines show a course quite
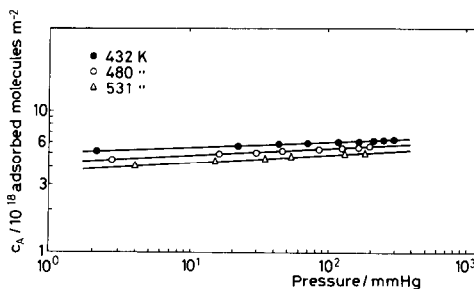

FIG. 1. Linear plots of Freundlich equation for CO_2 adsorption on $LaFeO_3$.

parallel and the pressure calculated for coverage equal to 1 is rather high. Isotherms of this type were also observed by Otto and Shelef (*5*) for adsorption of NO on oxidized Cr_2O_3 supported on alumina. As illustration, experimental results for N_2 adsorption on Sc_2O_3 between 113 and 323 K, from a previous work (*8*), are also given in Fig. 2. An adsorption for monolayer coverage of 6 $\times 10^{18}$ molec m^{-2} at a pressure of 26 atmospheres was found.

The materials used in adsorption and catalysis, generally, have a heterogeneous surface. Representative examples of this are perovskite-type oxides whose stoichiometry strongly depends on pretreatment conditions. At the temperature used for their preparation (*13*), nonstoichiometric compounds with excess ($LaFeO_{3+\alpha}$) or defect ($LaCoO_{3-\delta}$) of oxygen, giving place to transition ions with different oxidation states, are formed (*14*). On the other

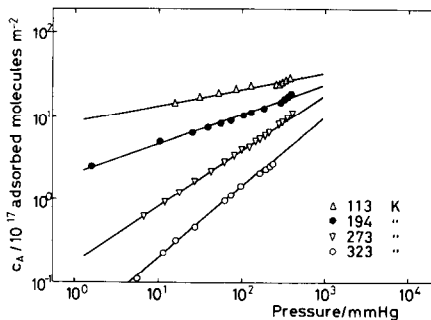FIG. 2. Linear plots of Freundlich equation for N_2 adsorption on Sc_2O_3. (Reproduced with permission from Ref. (*8*)).

TABLE 1

Values of Specific Surface Area as Calculated by the BET Method and from Freundlich Monolayer

Adsorbent	Adsorptive	Adsorptive's cross section ($\mathring{A}^2$ molec^{-1})[a]	Temperature of isotherms (K)	Surface area (m^2 g^{-1})		Reference
				BET method[b]	Freundlich monolayer	
$LaFeO_3$	CO_2	17	432, 480, 531	15.7	13.7	This work
$LaCoO_3$	CO_2	17	623, 673	15.5	15.0	(11)
$LaCoO_3$	O_2	14.1	423, 473, 523, 573, 623	15.5	17.0	(10)
Sc_2O_3	N_2	16.2	113, 195, 273, 323	11.8	11.5	(8)
Sc_2O_3	CO	16.8	77, 142, 195	16.4	16.5	(9)
Sc_2O_3	N_2O	20.4	195, 243, 273, 373, 573	12.5	15.3	(7)

[a] 1 $\mathring{A}^2 = 10^{-20}$ m^2.

[b] Adsorption of N_2 at 77 K; 16.2 $\mathring{A}^2$ for N_2 cross section.

hand, the breadth of the ir bands observed after adsorption of CO (15) and CO_2 (11) on $LaCoO_3$, due to mono- and bidentate carbonates of different kinds, also reflects surface heterogeneity. In the adsorption systems included in this work (Table 1) an exponential decrease of the adsorption heat with coverage was experimentally observed, even at low temperatures (113 K for N_2/Sc_2O_3 (8); 194 K for N_2O/Sc_2O_3 (7)). On the basis of the satisfactory fits obtained for Eq. (1), it can be concluded that the Freundlich model is the one that best describes the physical picture of the adsorption systems reported here.

In Table 1, values of specific surface areas (column 5) calculated by the BET method (N_2 adsorption at 77 K; 16.2 $\mathring{A}^2$ for N_2 cross section), and also values obtained from the Freundlich monolayer (column 6) for the system $CO_2/LaFeO_3$, are given. Data calculated from previous works (7–11) are also included. For N_2, CO, O_2, and CO_2, cross sections (column 3) calculated by Emmett (16) using the density of the adsorbate in the liquid state were taken. For N_2O, the cross section given by Livingstone (17) was used. As it can be observed, the values obtained from both methods are similar. The largest discrepancy was found for the N_2O/Sc_2O_3 system (22%). The equilibrium data were obtained, in this case, below 130 N m^{-2} and, consequently, low

coverages were reached. In order to obtain reliable data, it is advisable to analyze isotherms belonging to a descending branch of the isobar (see the work of Otto et al. (5)). An ascending nonequilibrium branch may yield inaccurate results.

The Freundlich equation may have an important potential application in supported oxides for which the active phase was found to be dispersed on the support as a bidimensional layer, when the temperatures used in the catalyst preparation are moderately high (18). However, to establish, unambiguously, the scope of validity of Eq. (1) and its usefulness for evaluation of the adsorption monolayer and of specific surface areas, more experimental work will be needed.

REFERENCES

1. Emmett, P. and Brunauer, S., J. Amer. Chem. Soc. 59, 310, 1553 (1937); J. Amer. Chem. Soc. 62, 1732 (1940).
2. Bridges, J. M., McIver, D. S., and Tobin, H. H., "Actes 2eme Congr. Intern. Catalysis, 1960" (Technip, Ed.), Vol. 2, p. 2161, 1961.
3. Parekh, B. S., and Weller, S. W., J. Catal. 37, 100 (1977); García Fierro, J. L., Mendioroz, S., Pajares, J. A., and Weller, S. W., J. Catal. 65, 263 (1980).
4. Thomas, J. M., and Thomas, W. J. "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, London, 1967.
5. Otto, K., and Shelef, M., J. Catal. 14, 226 (1969);

18, 184 (1970); **29,** 138 (1973). Gandhi, H. S., and Shelef, M., *J. Catal.* **24,** 241 (1972); **28,** 1 (1973).

6. Rudnitsky, L. A., and Alexeyev, A. M., *J. Catal.* **37,** 232 (1975).

7. González de Prado, J. E., Moreno, J., and Pajares, J. A., *An. Quim.* **71,** 477 (1975).

8. Tascón, J. M. D., González Tejuca, L., García Fierro, J. L., and Pajares, J. A., *An. Quim. Sup.* **1,** 70 (1978).

9. González de Prado, J. E., González Tejuca, L., Pajares, J. A., and Soria, J., *Act. Cient. Venez.* **24,** 189 (1973).

10. Tascón, J. M. D., and González Tejuca, L., *Z. Phys. Chem. Neue Folge* **121,** 79 (1980).

11. Tascón, J. M. D., and González Tejuca, L., *J. Chem. Soc. Faraday Trans. I* **77,** 591 (1981).

12. Courty, P. H., Ajot, H., Marcilly, C. H., and Delmon, B., *Powder Technol.* **7,** 21 (1973).

13. Tascón, J. M. D., Mendioroz, S., and González Tejuca, L., *Z. Phys. Chem. Neue Folge* **124,** 109 (1981).

14. Voorhoeve, R. J. H., Remeika, J. P., and Trimble, L. E., *Ann. N.Y. Acad. Sci.* **272,** 3 (1976).

15. Tascón, J. M. D., and González Tejuca, L., *Z. Phys. Chem. Neue Folge* **121,** 63 (1980).

16. Emmett, P. H., "Catalysis" (P. H. Emmett, Ed.), Vol. I. Reinhold, New York, 1954.

17. Livingstone, H. K., *J. Colloid. Sci.* **4,** 447 (1949).

18. Roozeboom, F., Fransen, T., Mars, P., and Gellings, P. J., *Z. Anorg. Allg. Chem.* **449,** 25 (1979).

Ma. A. Martín
J. M. D. Tascón
J. L. García Fierro
J. A. Pajares
L. González Tejuca

Instituto de Catálisis y Petroleoquímica,
CSIC,
Serrano 119, Madrid 6, Spain