

Physicochemical Properties of LaMnO₃: Reducibility and Kinetics of O₂ Adsorption

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The kinetics of reduction in H₂ of the perovskite LaMnO₃ and also the kinetics of O₂ adsorption on this oxide were studied. The reduction process starts at 755 K; up to 950 K the reduction rate is low because of the slowness of nuclei formation and growth (nucleation). Once reduced nuclei are formed, the reduction process occurs at a higher rate (950–1050 K). At 1100 K a stable reduced state of ca. 1e⁻ per molecule, accompanied by the disappearance of the perovskite structure and formation of La₂O₃ and MnO, was reached. The reduction isotherms (873–1013 K), of sigmoidal form are typical of a reduction process controlled by formation and growth of reduction nuclei on the surface. An apparent activation energy of reduction of ca. 225 kJ mol⁻¹ was found. The kinetics of O₂ adsorption showed (by means of plots $b(dq/d \ln t)$ vs at) an Elovichian zone preceded (followed) by pre- and post-Elovichian regions. The results were fitted to a model of adsorption on a heterogeneous surface developed by M. Ungarish and C. Aharoni (*J. Chem. Soc. Faraday Trans. I* 79, 119, 1983). The isobar of adsorption showed, in the range 350–700 K, two different activated processes which were associated to dissociative adsorption of oxygen (350–525 K) and incorporation of oxygen into the oxide lattice (above 600 K). A parallelism among oxygen adsorption, reducibility, and catalytic activity for total oxidation on LaMeO₃ oxides was found.

INTRODUCTION

Within the first-row transition metal oxides LaMeO₃ with perovskite-type structure, LaMnO₃ is one of the most active catalysts for CO oxidation (1). Experiments carried out in this laboratory indicate that this high activity applies also to total oxidation of C₃ and C₄ hydrocarbons. Partially substituted LaMnO₃-based catalysts have been widely used for these reactions (2).

High adsorption of oxygen has been associated with high activity for total oxidation processes on simple (3) and mixed (4) oxides. On the other hand, LaCoO₃ has a high oxidation activity while LaCrO₃ showed low activity. This seems to indicate a certain correlation between oxygen adsorption on these oxides and their reducibility. These properties should be of interest for the study of the catalytic behavior of these materials.

As part of a more comprehensive study on the surface properties of LaMeO₃ ox-

ides, in this work, the reducibility of LaMnO₃ and the kinetics of O₂ adsorption on this oxide were investigated. The experimental results were analyzed according to a kinetic model of adsorption on a heterogeneous surface and compared with data obtained on similar systems.

EXPERIMENTAL

Sample preparation and gases. LaMnO₃ was prepared by amorphous precursors (citrate) decomposition as described by Courty *et al.* (5). Briefly, to an equimolecular solution of metal nitrates (La(NO₃)₃ · 6H₂O and Cr(NO₃)₃ · 9H₂O, both reagent grade from Merck) a solution of citric acid monohydrate (reagent grade from Merck) was added so that the ratio of gram-equivalents of acid to total gram-equivalents of metals was equal to 1. The water was evaporated at 343 K in a rotary evaporator until the precipitate acquired the consistency of a viscous syrup. The precursor so obtained was kept in a vacuum stove at 373 K for 5 h and then calcined at 973 K for 5 h. The

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presence of a single perovskite phase was verified by means of thermogravimetric analysis and X-ray diffraction. A typical X-ray pattern of the final product is given in Fig. 1a. A sample obtained by oxalates decomposition at 1173 K gave a similar pattern. As it can be observed, peaks of simple oxides of La or Mn are absent. More details of preparation were given elsewhere (6). The sample had a BET specific surface area (0.162 nm² for cross-sectional area of N₂ molecule) of 12.1 m² g⁻¹.

H₂ (99.995% pure) for reducibility and O₂ (99.98% pure) for adsorption experiments were from Sociedad Española del Oxígeno. Before storage they were purified by standard methods.

Equipment and methods. Kinetic experiments of reduction or of O₂ adsorption were carried out by means of a Cahn 2100 RG microbalance (sensitivity 1 μg) connected to a high-vacuum line capable of attaining a dynamic vacuum of 10⁻⁶ mmHg (1 mmHg = 133.3 N m⁻²). For reducibility runs, a 70-mg sample was first pumped at room tem-

perature (r.t.) for 1 h, heated at 4 K min⁻¹ up to the reduction temperature (873–1013 K) and then contacted with 300 mmHg H₂. The weight loss as a function of time (*t*) was recorded until no significant weight change was observed. The reduced sample was then pumped at the reduction temperature for 0.5 h, reoxidized in purified air (free of H₂O or CO₂) at 873 K for 1 h and cooled down to r.t. After this treatment the sample regained its initial weight. A temperature-programmed reduction (TPR) experiment (heating rate 4 K min⁻¹) was also carried out. In this case, after pumping at r.t. for 1 h, the sample was contacted with 300 mmHg H₂ and the experiment started. The weight loss recorded was taken as a measure of the extent of reduction in terms of electrons (*e*⁻) per molecule (the maximum reduction degree, 3*e*⁻ per molecule, would correspond to reduction of Mn³⁺ to metallic manganese).

Prior to an experiment of kinetics of O₂ adsorption, the LaMnO₃ sample (250 mg) was outgassed at 773 K for 15 h and then cooled to the desired temperature. After this O₂ was introduced in the microbalance enclosure and the kinetic curve of adsorbed oxygen (*q*) vs time (*t*) recorded. Two series of experiments were carried out: At constant pressure (25 mmHg O₂) and variable temperature (301 to 685 K) and at constant temperature (473 K) and variable pressure (0 to 100 mmHg O₂). In the first series, weight changes were recorded for 2 h and also after the system O₂/LaMnO₃ reached equilibrium. In the second series, kinetic curves were recorded for 20 min. From these, initial adsorption rates, *r*₀, were calculated by fitting the data to a polynomial function and differentiation to *t* = 0.

X-Ray diffraction patterns were obtained with a Philips PW/1010 diffractometer using CuKα radiation and a Ni filter.

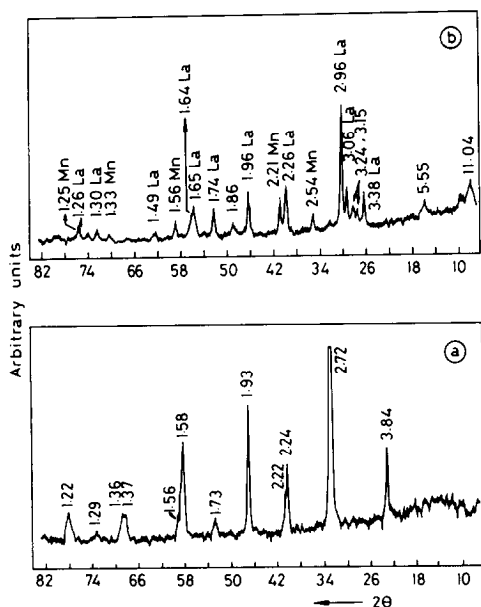


FIG. 1. X-Ray diffraction patterns (CuKα radiation) of a sample of LaMnO₃ before (a) and after (b) reduction at 993 K in H₂. The *d* is in Å (1 Å = 0.1 nm). La and Mn stand for La₂O₃ and MnO, respectively.

RESULTS

Temperature-Programmed Reduction

TPR results between r.t. and 1173 K are

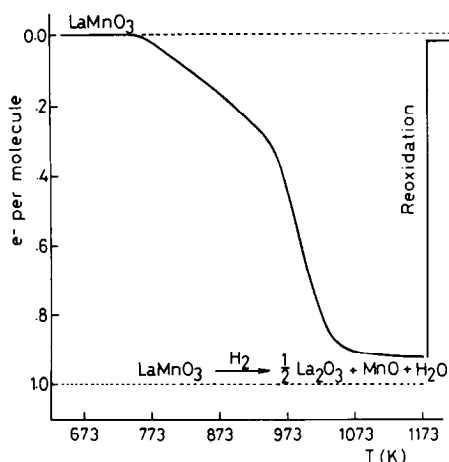


FIG. 2. Temperature-programmed reduction (300 mmHg H_2) of LaMnO_3 (heating rate 4 K min^{-1}).

represented in Fig. 2. As it can be observed the reduction starts at 755 K. From this temperature up to 950 K, the reduction rate is low because of the slowness of nuclei formation and growth (nucleation). Once reduced nuclei are formed the reduction process occurs at a higher rate (950–1050 K). Above 1050 K the reduction curve levels off and a stable reduced state of about $1e^-$ per molecule is reached. By reoxidation at 873 K in purified air (1 h) the initial weight was practically regained (Fig. 2).

Isothermal Reduction

Taking as a basis the TPR results (Fig. 2)

the kinetics of LaMnO_3 reduction in H_2 (300 mmHg) at temperatures of 873 to 1013 K was studied. The plots $e^- \text{ molec}^{-1}$ vs t (Fig. 3), present a sigmoidal form typical of a reduction process controlled by formation and growth of reduction nuclei on the surface followed by reduction in the bulk. The time corresponding to the inflection of the curves indicates the point where these nuclei start advancing from the surface to the bulk. These plots point to a common reduction degree of about $0.93 e^- \text{ molec}^{-1}$. The time required for attaining this reduction level drastically decreased with increasing temperature. On the other hand, the increase of the initial reduction rate with temperature shows that this is an activated process.

The color of the sample, initially black, became grey after reduction suggesting that new phases were present. To confirm this, after the experiment at 993 K, the sample was cooled down in H_2 (to prevent reoxidation) to r.t. and then an X-ray diffraction pattern was obtained (Fig. 1b). This showed the disappearance of the perovskite structure with formation of isolated La_2O_3 and MnO phases. These results together with TPR data indicate that the reduction of lanthanum manganite takes place according to the reaction,

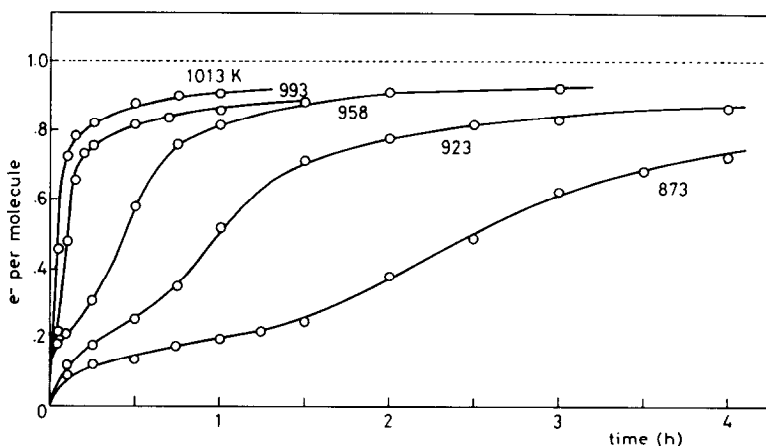


FIG. 3. Kinetic reduction isotherms of LaMnO_3 in 300 mmHg H_2 .

After the experiment at 873 K (Fig. 3) the reduced sample was oxidized at this temperature in air and its X-ray diffraction pattern (not shown) recorded. Peaks of La_2O_3 and Mn_2O_3 besides peaks (of very low intensity) of LaMnO_3 were found indicating that the reduction process is mainly irreversible at the reduction temperature.

Kinetics of Oxygen Adsorption

As said above two different sets of kinetic experiments were carried out. In the first one the effect of temperature on both the initial adsorption rate, r_0 at zero time, and the extent of O_2 adsorption (isobaric experiments) were studied. In the second one the effect of pressure on the initial adsorption rate (isothermal experiments) was studied.

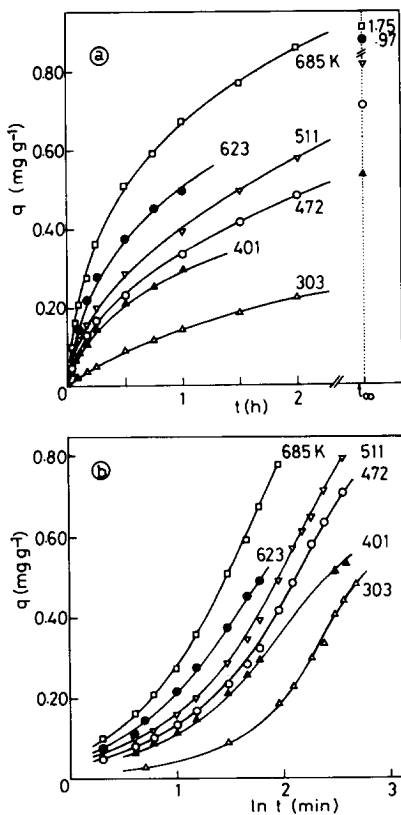


FIG. 4. Plots q vs t (a) and q vs $\ln t$ (b) of integral kinetic data of adsorption of O_2 (25 mmHg) on LaMnO_3 at different temperatures.

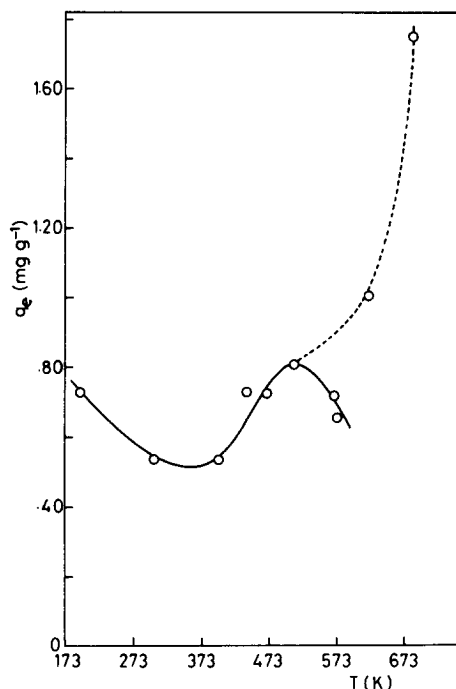


FIG. 5. Isobar of adsorption of O_2 on LaMnO_3 at 25 mmHg.

The integral kinetic data q vs t at 25 mmHg and temperatures of 303 to 685 K are given in Fig. 4a. The adsorption recorded at equilibrium (q_e , at t_∞) is also given. Both r_0 and q_e increase with temperature showing the existence of an activated process. The time required to reach equilibrium of adsorption was rather high particularly at higher adsorption temperatures (e.g., at 303 and 685 K, 8 and 32 h, respectively, were needed).

Adsorption data at equilibrium (at 25 mmHg) as a function of temperature are given in Fig. 5; in this plot the adsorption at dry-ice temperature was also included. In the range 195 to 350 K, q_e decreases with increasing temperature indicating an adsorption which occurs with no activation energy. Between 350 and 525 K (first ascending branch) activated adsorption occurs. At 573 K an adsorption lower than that at 525 K was observed (this experiment was duplicated). Above 600 K q_e increases sharply with temperature (second ascend-

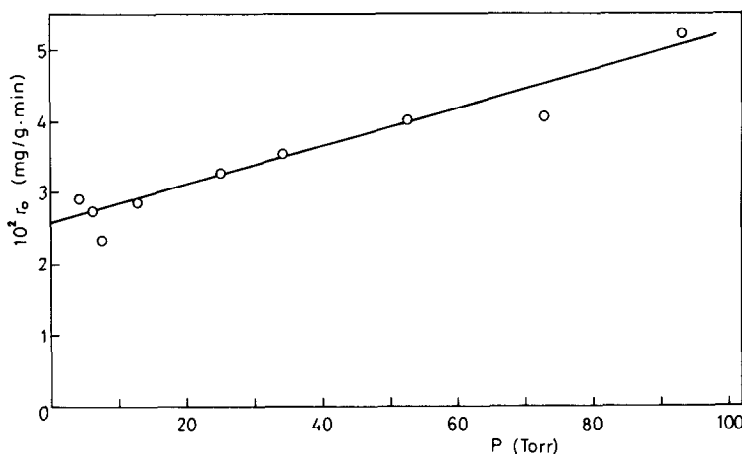


FIG. 6. Initial adsorption rate (r_0) as a function of pressure.

ing branch). These results suggest the appearance at higher temperatures of a process with an activation energy higher than that of the process which takes place at 350–525 K.

Values of r_0 as a function of oxygen pressure (P) at 473 K and 0–100 mmHg are represented in Fig. 6. A linear dependence of r_0 with P , similar to that found for the system CO/LaCrO_3 (7) was observed.

DISCUSSION

Reducibility

Tofield and Scott (8) and Vogel *et al.* (9) found oxidative nonstoichiometry ($\text{LaMnO}_{3.11-3.13}$) in lanthanum manganite samples where calcination temperatures of 1373 K and above were used. These last authors observed in the temperature-programmed reduction (heating rate 20 K min^{-1}) of $\text{LaMnO}_{3.13}$ an intermediate reduced state, very stable in a wide range of temperatures (773–1173 K), corresponding to stoichiometric LaMnO_3 . The final reduction to La_2O_3 and MnO occurred between 1173 and 1325 K (9). The TPR curve in Fig. 2 shows that, in our preparation, the reduction, up to $1e^-$ per molecule, takes place in one single step at temperatures substantially lower than those given by Vogel *et al.* (9). On the other hand, the weight loss recorded and the X-ray diffraction pattern in

Fig. 1b indicate a reduction of about $1e^-$ molec^{-1} with formation of La_2O_3 and MnO . These findings suggest that the starting sample should be LaMnO_3 (without excess of oxygen) with similar characteristics to these given by Johnson *et al.* (10) for substitute lanthanum manganites calcined at the same temperature (973 K) to that used in this work.

The kinetic data in Fig. 3 were analyzed according to Avrami–Erofeev's equation (11) which describes isothermal reactions in a very wide range of transformation ($0.05 \leq \alpha \leq 0.90$),

$$1 - \alpha = \exp(-kt^n) \quad (1)$$

where α is the reduction degree and n and k are temperature-dependent constants. From the slopes and origin ordinates of the family of straight lines $-\ln[\ln(1 - \alpha)]$ vs $\ln t$ (linearized form of Eq (1)), n and k were calculated. Their values are given in Table 1. As it can be observed, n varies little with T indicating that the mechanism of nuclei growth is not affected in any significant way by the temperature. The apparent activation energy of reduction (E_{red}) of LaMnO_3 , as calculated from $\ln k$ vs $1/T$ plots (Fig. 7) (in isothermal conditions k does not depend on the reduction degree), was found to be 247 kJ mol^{-1} . As the kinetic curves of reduction exhibited a sigmoidal shape (the exact form of each one is determined by the

TABLE I
Kinetic Parameters of Reduction

T (K)	$t_{0.5}^a$ (h)	$t_{0.5}^{-1}$ (h ⁻¹)	n	k
873	2.21	0.45	1.25	1.34×10^{-3}
923	0.92	1.08	1.17	6.57×10^{-3}
958	0.40	2.50	1.14	1.69×10^{-2}
993	0.14	7.11	1.10	5.45×10^{-2}
1013	0.04	24.40	1.11	1.78×10^{-1}

^a Time required to attain a reduction of $0.5 e^- \text{ molec}^{-1}$.

changing geometry of the gas–solid interface), E_{red} was also calculated from the plot $\ln(1/t_{0.5})$ vs $1/T$ (11) (Fig. 7) ($t_{0.5}$, time required to attain a reduction degree of $0.5 e^- \text{ molec}^{-1}$). In this case a value of 200 kJ mol^{-1} was found.

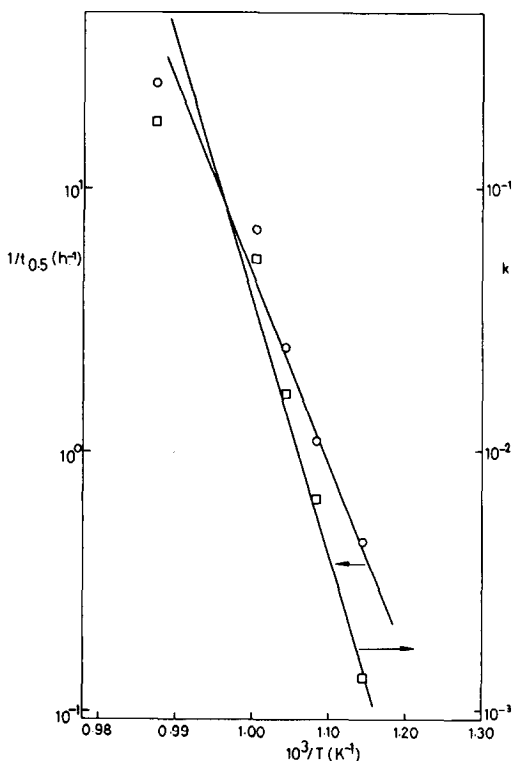


FIG. 7. Arrhenius plots of k (constant of Avrami-Erofeev's equation, Table I) and $1/t_{0.5}$ ($t_{0.5}$, time required for a reduction of $0.5 e^- \text{ molec}^{-1}$) vs $1/T$.

Kinetics and Equilibrium of O_2 Adsorption

The kinetic curves of O_2 adsorption in the interval 303–685 K (Fig. 4a) represented in coordinates q vs $\ln t$ (Fig. 4b) had a sigmoidal shape which is typical of a kinetic process of activated adsorption. In the region of maximum slope (around the inflection point) the plots are frequently linear and in this part an Elovichian kinetics of adsorption is obeyed. This region is preceded by a concave part and followed by a convex part which correspond to pre-Elovichian and post-Elovichian regions, respectively. Aharoni and Ungarish (12) deduced the existence of these regions from the sigmoidal form of t vs $(dq/dt)^{-1}$ curves. These regions are also clearly shown when kinetic data are represented as $dq/d \ln t$ vs t plots. As

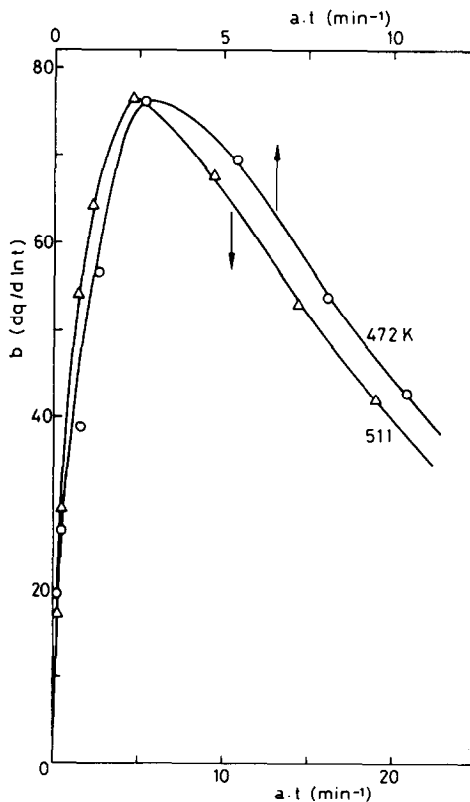


FIG. 8. Plots of $b (dq/d \ln t)$ vs $a.t$ for O_2 adsorption on LaMnO_3 ; q in mg g^{-1} . a (472 K) = 4.75×10^{-5} , a (511 K) = 2.7×10^{-5} in min^{-1} ; b (472 K) = 8.950×10^{-4} , b (511 K) = 8.975×10^{-4} , in mg .

illustration, kinetic data at 472 and 511 K were represented in these coordinates, in Fig. 8. In these volcano plots the ascending and descending branches correspond to the pre-Elovichian and post-Elovichian parts. The rather sharp maxima indicate that, in these cases, the Elovichian region is not predominant. Ungarish and Aharoni showed in a recent analysis (13) that the adsorption systems $\text{H}_2/\text{Sc}_2\text{O}_3$ and O_2/W exhibited a similar kinetic behavior.

The quantitative description of kinetic data was made taking as a basis a model of adsorption on a heterogeneous surface (13). In it, it is assumed that the adsorbent surface comprises a large number of homogeneous patches characterized by a given value of the energy of adsorption, H , constant for a given patch and varying from patch to patch. Taking into account that the activation energy of adsorption, E_a , in a patch is given by the equation

$$E_a - \alpha H = RT \ln (\beta \theta + \gamma) \quad (2)$$

(θ , coverage; α and γ constants) and assuming that desorption is negligible, the following integrated equation is derived:

$$-\ln (1 - \theta) - \theta = t/\tau \exp(-\alpha H) \quad (3)$$

(τ , constant inversely proportional to the adsorption constant).

The kinetic data for isobaric runs given in Fig. 4 were represented, according to Eq. (3), in Fig. 9. All the linear transforms pass through the origin. For temperatures of 303

to 511 K, the experimental results fit satisfactorily Eq. (3) (at higher temperatures and large times the experimental points scatter somewhat from the straight line). This is in agreement with previous results which showed that the surface of LaMeO_3 perovskite-type oxides is highly heterogeneous (14). From a plot $\ln r_0$ vs $1/T$ an activation energy of adsorption of 16 kJ mol^{-1} , equal to that calculated for the system $\text{O}_2/\text{LaCrO}_3$ (15) was found.

FINAL REMARKS

Coverages of oxygen at 25 mmHg on LaCoO_3 (4), LaCrO_3 (15) and LaMnO_3 in the temperature range 300–700 K are given in Table 2. As it can be observed, they decrease from LaCoO_3 to LaCrO_3 . On the other hand, remarkable differences in reducibility (in H_2) were observed among these oxides: LaCoO_3 reached a reduction level of $1e^- \text{ molec}^{-1}$ at 673 K and full reduction to $3e^- \text{ molec}^{-1}$ at 773 K (16). For LaMnO_3 temperatures of about 1070 K were needed for a reduction of $1e^- \text{ molec}^{-1}$. At 1170 K LaCrO_3 was only reduced to $10^{-2} e^- \text{ molec}^{-1}$ (15). Therefore, the adsorption of O_2 on these oxides as well as their reducibility follow the same sequence of the catalytic activity found for CO oxidation: $\text{LaCoO}_3 > \text{LaMnO}_3 > \text{LaCrO}_3$ (1). This finding is in agreement with earlier results of Meadowcroft (17). These differences in adsorption and catalytic properties must be related to the transition metal cation (La^{3+} is a poor adsorbent of O_2). The outgassing treatment underwent by the samples (15 h at 773 K) prior to an adsorption experiment produces a higher concentration of oxygen vacancies on the adsorbent surface and this causes the O_2 adsorption to be higher on the most reducible oxides.

Coverages of adsorbed oxygen on LaMnO_3 (taking as cross-sectional area of O_2 molecule, 0.141 nm^2) (18) in the first ascending branch of the isobar range from 0.12 (300 K) to 0.20 (600 K) (Table 2). How-

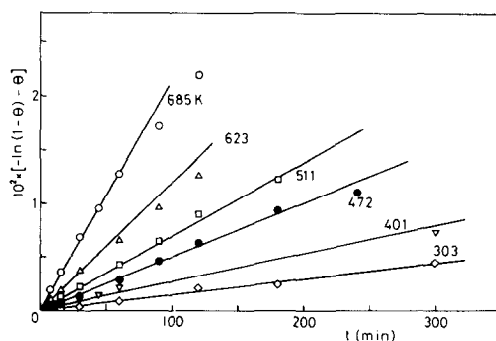


FIG. 9. Plots of integral kinetic data in Fig. 4 according to Eq. (3) (see text).

TABLE 2

Coverages of O₂ on LaMeO₃ Oxides^a

	T/K				
	300	400	500	600	700
LaCoO ₃	0.10	0.36	0.34	0.23	0.24
LaMnO ₃	0.12	0.12	0.17	0.20	—
LaCrO ₃	0.01	0.03	0.11	0.17	0.13

^a Cross-sectional area of O₂ molecule, 0.141 nm².

ever, the adsorption at 685 K amounts to a coverage of 0.38. This, together with the form of the isobar (Fig. 5, two ascending branches separated by an inflection) strongly suggest that in the temperature range 350–700 K two very different chemical processes occur. Taking on account that at 400 K LaMnO₃ becomes catalytically active for CO oxidation, the activation underwent by the O₂ molecule at 350–525 K should be related to oxygen chemisorption as O⁻ through O₂⁻ as observed in the system O₂/LaCoO₃ (4). The high coverages obtained above 600 K must be related to incorporation of oxygen into the oxide lattice. The adsorption of oxygen on LaCoO₃ (easily reducible oxide) also presented an isobar with a second ascending branch above 600 K (4), although not as pronounced as that found in the system O₂/LaMnO₃. On the contrary, in the adsorption of O₂ on LaCrO₃ (oxide difficult to reduce) this behavior was not observed (14).

REFERENCES

1. Tascón, J. M. D., and González Tejuca, L., *React. Kinet. Catal. Lett.* **15**, 185 (1980).
2. Gallagher, P. K., Johnson, Jr., D. W., and Schrey, F., *Mater. Res. Bull.* **9**, 1345 (1974); Yao, Y.-F. Y., *J. Catal.* **36**, 266 (1975); Voorhoeve, R. J. H., Johnson, Jr., D. W., Remeika, J. P., and Gallagher, P. K., *Science* **195**, 827 (1977).
3. Iwamoto, M., Yoda, Y., Yamazoe, N., and Seiyama, T., *J. Phys. Chem.* **82**, 2564 (1978).
4. Tascón, J. M. D., and González Tejuca, L., *Z. Phys. Chem. Neue Folge* **121**, 79 (1980).
5. Courty, Ph., Ajot, H., Marcilli, Ch., and Delmon, B., *Powder Technol.* **7**, 21 (1973).
6. Tascón, J. M. D., Mendioroz, S., and González Tejuca, L., *Z. Phys. Chem. Neue Folge* **124**, 109 (1981).
7. Fierro, J. L. G., and González Tejuca, L., *J. Colloid Interface Sci.* **96**, 107 (1983).
8. Tofield, B. C., and Scott, W. R., *J. Solid State Chem.* **10**, 183 (1974).
9. Vogel, E. M., Johnson, Jr., D. W., and Gallagher, P. K., *J. Amer. Ceram. Soc.* **60**, 31 (1977).
10. Johnson, Jr., D. W., Gallagher, P. K., Schrey, F., and Rhodes, W. W., *Amer. Ceram. Soc. Bull.* **55**, 520 (1976).
11. Keatch, C. J., and Dollimore, D., "An Introduction to Thermogravimetry," 2nd ed., Chap. 5. Heyden, London, 1975.
12. Aharoni, C., and Ungarish, M., *J. Chem. Soc. Faraday Trans. 1* **72**, 400 (1976).
13. Ungarish, M., and Aharoni, C., *J. Chem. Soc. Faraday Trans. 1* **79**, 119 (1983).
14. González Tejuca, L., Rochester, C. H., Fierro, J. L. G., and Tascón, J. M. D., *J. Chem. Soc. Faraday Trans. 1* **80**, 1089 (1984).
15. Fierro, J. L. G., and González Tejuca, L., *J. Catal.* **87**, 126 (1984).
16. Crespín, M., and Hall, W. K., *J. Catal.* **69**, 359 (1981).
17. Meadowcroft, D. B., *Nature (London)* **226**, 847 (1970).
18. Emmett, P. H., "Catalysis," Vol. 1, Chap. 2. Reinhold, New York, 1954.