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Catalysis of Carbon Monoxide Oxidation by Cerium Dioxide

II. Microcalorimetric Investigation of Adsorption and Catalysis

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Adsorption and catalytic properties of ceria surfaces towards carbon monoxide oxidation have been investigated by microcalorimetry. Results are interpreted assuming that the defect structure of the catalyst is single-phased, and that its catalytic action consists of successive oxidations and reductions of its surface.

I. INTRODUCTION

Catalysis of carbon monoxide oxidation by CeO_2 and the related interactions of the gaseous components have been investigated, and results obtained by gravimetry, infrared spectroscopy and kinetic study of the reaction have been reported elsewhere (*1, 2*). The present paper, which constitutes the second part of the work already presented in Part I (*2*), deals with the application of microcalorimetry to this system.

II. EXPERIMENTAL METHODS

A. Materials

All the gases used contained less than 50 vol/million of impurities. Cerium dioxide was prepared by thermal decomposition in air of $(NH_4)_2Ce(NO_3)_6$ at 500°C during 24 hr. Prior to any experiment, the solid was submitted to one of the following treatments:

Heating in air at 450°C during 4 hr, then under vacuum (10^{-5} Torr) at the same temperature during 16 hr. Catalyst obtained from this treatment is designated by "ceria A." Its composition, as determined by chemical analysis, corresponded to $CeO_{1.985(\pm 0.003)}$. In the sequel, the amount of oxygen in the formula is designated by x and its variations by Δx.

After this treatment, heating under hydrogen (200 Torr, 450°C, during 5 hr), then under vacuum (10^{-5} Torr, during 16 hr) gave rise to a solid designated "ceria B." Its chemical composition corresponded to $CeO_{1.945(\pm 0.003)}$.

Both A and B samples exhibited a specific surface area of 27 m^2/g.

B. Apparatus

Differential heats have been measured with a thermocouple calorimeter to which a volumetric setup has been adapted, according to a technique which has already been described (*3–5*). In all reported experiments, the catalyst mass was 500 mg. The temperature range was comprised between 200 and 300°C. The expected error in the heat determination depends on the duration of interaction between the solid and the gaseous phase. It can be estimated at 5% for the adsorption experiments, and 10% for the catalysis experiments. In the sequel, the experimental heats will be designated by Q, expressed in kcal/mole and, for convenience, considered as positive for a heat liberated by the reacting system, which corresponds to the majority of the investigated cases. When we deal with theoretical expressions of the heat evolved

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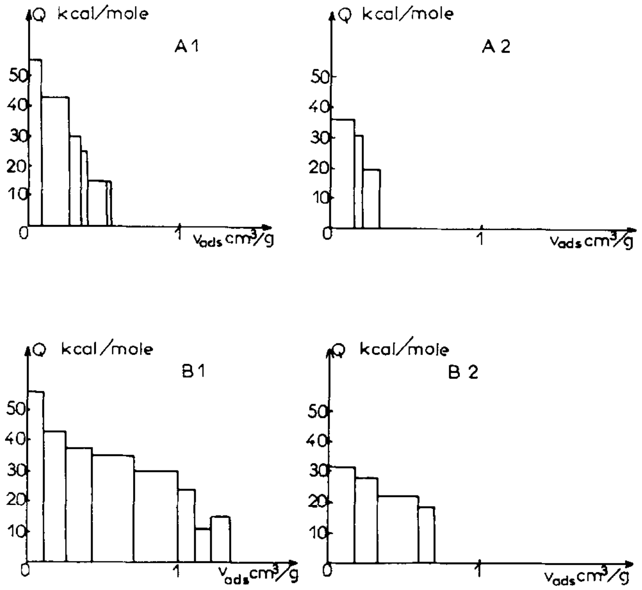


FIG. 1. CO_2 adsorption on CeO_2 at 300°C (calorimetric patterns): (A1) first adsorption on CeO_2 A; (A2) second adsorption on CeO_2 A; (B1) first adsorption on CeO_2 B; (B2) second adsorption on CeO_2 B.

by a reaction, the usual symbols ΔU and ΔH will be used, with the converse sign convention.

III. RESULTS

A. Carbon Dioxide Adsorption

Results of carbon dioxide adsorption on ceria samples A and B are sketched in Fig. 1 for the heat evolved ("calorimetric" isotherm), and in Fig. 2 for the variation on the adsorbed volume with the logarithm of the adsorbate pressure ("volumetric" isotherm).

Ceria A. When after a first CO_2 chemisorption at 300°C and a subsequent evacuation (at the same temperature, under 10^{-5} Torr, during 16 hr) further CO_2 amounts are contacted anew with the solid, the differential chemisorption heat does not appreciably change (except for its initial value). On the volumetric isotherm both series of measures practically fit on the same straight line (Curve a). This can be explained by the fact that, after the evacuation, only a very small CO_2 fraction remains adsorbed.

Ceria B. Ceria B behaves differently, though its specific area is the same as that of ceria A. The amount adsorbed for the first time, is about three times larger than the CO_2 amount adsorbed under the same conditions on ceria A. Moreover, the volume adsorbed with a heat larger than 35 kcal/mole is almost five times what it was on ceria A. Both volumetric and calorimetric isotherms show a break after the fourth increment.

When after an evacuation (same temperature, 10^{-5} Torr, 16 hr) a second CO_2 adsorption is carried out, there is a different phenomenon: the volumetric curve c in Fig. 2 starts at a volume located 0.73 cm^3 under the starting point of curve b. This volume is about that adsorbed during the first four increments during the preceding adsorption, i.e., that adsorbed with a heat at least equal to 35 kcal/mole.

B. Oxygen Adsorption (Fig. 3)

On ceria A, the oxygen volume corresponding to a measurable heat is minute (0.06 cm^3/g). Further adsorptions are not accompanied by any heat evolution. On the contrary, introduction of successive amounts onto ceria B liberates a large heat

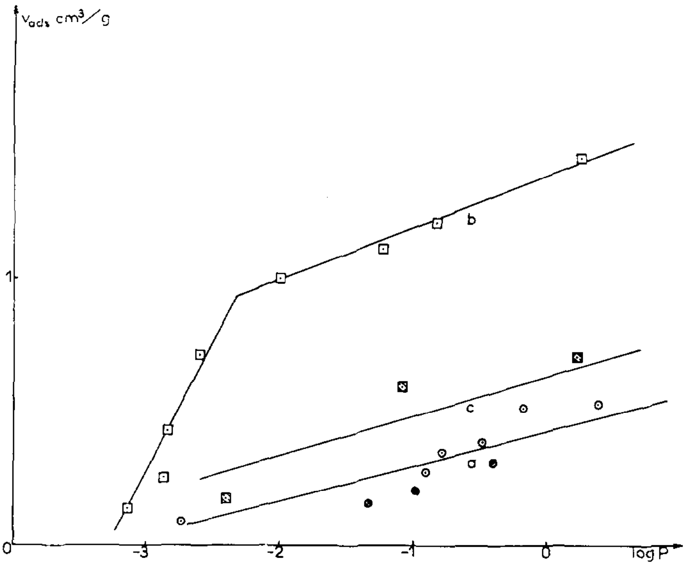


FIG. 2. CO_2 adsorption on CeO_2 (volumetric isotherms at 300°C): (⊙) first adsorption on CeO_2 A; (●) second adsorption on CeO_2 A; (⊡) first adsorption on CeO_2 B; (▨) second adsorption on CeO_2 B.

(initially equal to 110 kcal/mole at 300°C) until the fixed volume reaches 3.4 cm³/g. Beyond this volume, the evolved heat abruptly drops to a value close to the initial chemisorption heat on ceria A. Oxygen chemisorption corresponding to the large heat evolution is practically instantaneous and the residual equilibrium pressure is very low (10^{-4} Torr).

C. Carbon Monoxide Adsorption

Carbon monoxide interaction with ceria has been investigated between 200 and 300°C, but more especially at 300°C, when

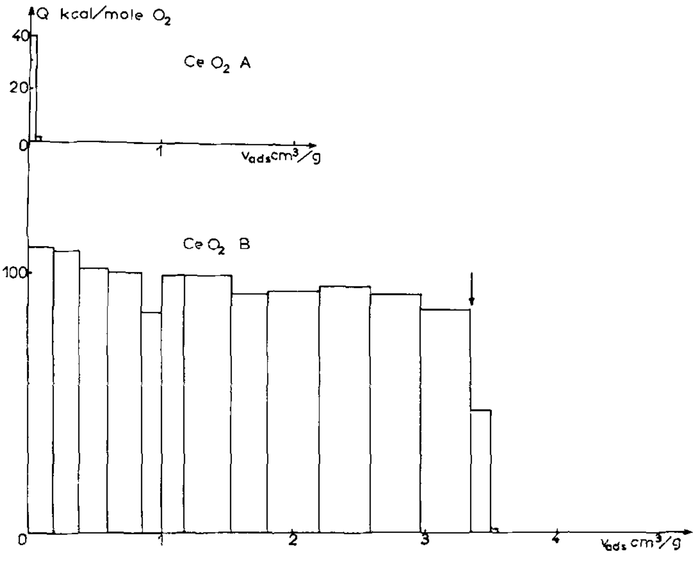


FIG. 3. Oxygen adsorption on ceria at 300°C.

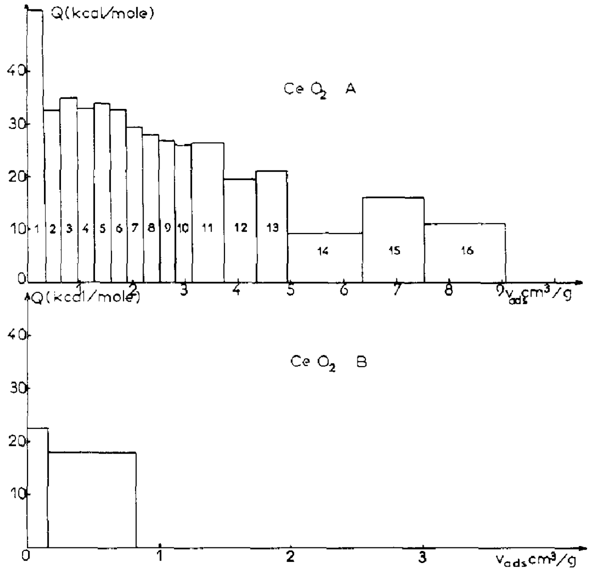


FIG. 4. Carbon monoxide adsorption on ceria, at 300°C (calorimetric patterns).

the reaction rate is rapid enough to allow an accurate determination of the evolved heat. The following results refer to 300°C and a CO pressure which always remains less than 2 Torr; no CO disproportionation can be detected under these conditions.

On ceria A, carbon monoxide reacts with an initial heat of 52.5 kcal/mole. The evolved heat is a rapidly decreasing function of adsorbed volume, the last amounts being adsorbed with a much lower heat (10 kcal/mole), as shown by the calorimetric curve in Fig. 4. The related volumetric curve (Fig. 5) exhibits two branches: the first one (a) corresponds to the first 13 increments and is rather steep,

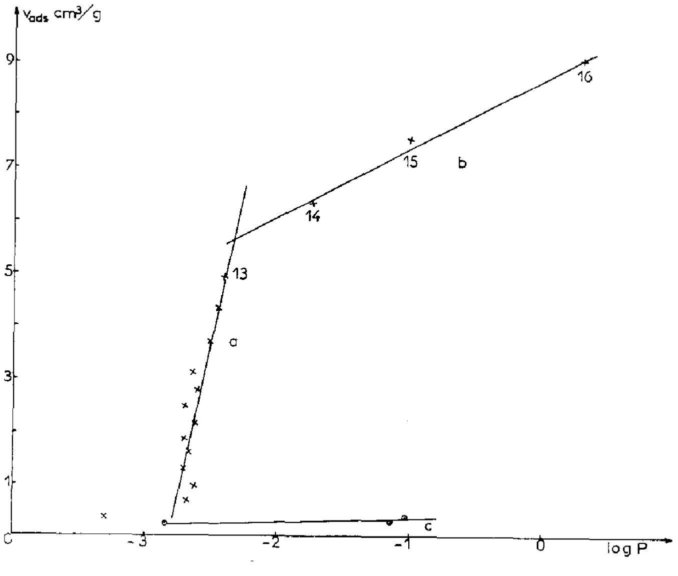


FIG. 5. Carbon monoxide adsorption on CeO_2 at 300°C (volumetric isotherms): (a and b) CeO_2 A; (c) CeO_2 B.

because the equilibrium pressures are close to each other and low; the second one (b) has a smaller slope, due to the fact that the equilibrium pressure appreciably rises after each introduction. A second adsorption after a degassing (300°C, 10^{-5} Torr, 16 hr) liberates 20 kcal/mole, i.e., the heat corresponding to the beginning of the second branch.

On ceria B, calorimetric and volumetric curves sketched in Fig. 4 and 5 (curve c) show a carbon monoxide adsorption of the second type.

D. Adsorption Sequence $CO + O_2$

After CO has been adsorbed on ceria A, an evacuation (300°C, 10^{-5} Torr, 16 hr) eliminates the reversibly adsorbed CO amount. Oxygen interaction with the resulting solid then exhibits the same characteristics (and especially the same exothermicity) as oxygen interaction with ceria B. The total amount of oxygen reacting with a heat evolution greater than 5 kcal/mole is equal to half of the irreversibly fixed CO amount. This ratio remains constant, whatever the temperature of CO and oxygen adsorptions (from 200 to 300°C).

A set of successive and alternate adsorptions of small amounts of CO and O_2 has been carried out, according to following process: (i) a volume v_1 of CO is reacted with the surface. The corresponding amount being irreversibly adsorbed, subsequent evacuation (300°C, 10^{-5} Torr, 16 hr) is not followed by any desorption; (ii) oxygen is then admitted until the heat evolved by the last addition is equal to 5 kcal/mole, which is considered as the lower limit for the heat corresponding to the strong adsorption of this adsorbate. Let v_2 be the total volume of oxygen admitted under these conditions. A further evacuation (300°C, 10^{-5} Torr, 16 hr) does not induce any desorption, all constituents being irreversibly adsorbed. The preceding cycle is then resumed.

TABLE 1
SUCCESSIVE AND ALTERNATE ADSORPTIONS OF CARBON MONOXIDE AND OXYGEN ON CERIA

v_1 (cm³/g)	v_2 (cm³/g)	$\frac{v_2}{v_1}$	Q_1 (kcal/mole CO)	Q_2 (kcal/mole O_2)
0.319	0.153	0.479	51	70
0.318	0.158	0.496	42	69
0.314	0.150	0.476	44	58
0.318	0.159	0.500	44	58
0.310	0.169	0.545	44	50

Table 1 shows the results, where Q_1 and Q_2 designate the average adsorption heats per mole of carbon monoxide and oxygen respectively. It can be seen from this table that the volume of adsorbed oxygen is always close to half of the volume of adsorbed CO, under these conditions.

E. Reaction $CO + \frac{1}{2}O_2$

Microcalorimetric investigation of carbon monoxide oxidation has been undertaken by introducing amounts of the stoichiometric reactant mixture to the ceria samples. Carbon dioxide is condensed in a liquid nitrogen trap located in the vicinity of the calorimetric cells. In spite of this arrangement, the heat evolved may differ from 68 kcal, which is close to the heat liberated at constant volume by the reaction:

$$CO_g + \tfrac{1}{2}O_{2g} \rightarrow CO_{2g}$$

as shown by Fig. 6, which corresponds to the reaction carried out on ceria A. This phenomenon has already been found with ThO_2 (*5*).

It is worth noting that on ceria B, heat evolution kinetics during an individual run greatly differ from that of ceria A: the time required for the pressure to return to a negligible value is considerably longer, but can be reduced by a subsequent admission of pure oxygen to the catalyst. For instance, at 300°C, the time required for a complete oxidation of 0.260 cm³ CO/g of ceria drops from 1383 min during the first run to 174 min after two sequences catalysis + oxidation. The latter time is of the order of that observed on ceria A.

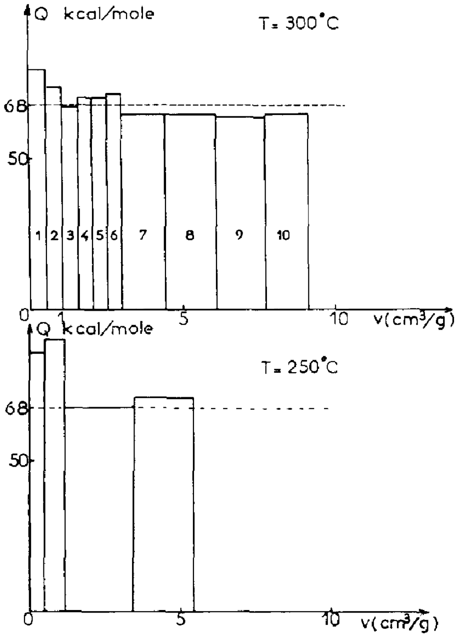


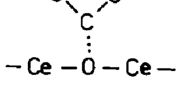
FIG. 6. Heat evolution during stoichiometric mixture reaction in the presence of CeO_2 A.

IV. DISCUSSION

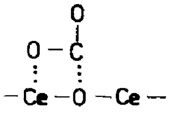
A. Carbon Dioxide Adsorption

Let us first stress the fact that although Elovich-type kinetics have been found for CO_2 adsorption (*1*), no absolute physical meaning is to be attached to the simplified Temkin-type representation of the volumetric isotherm in Fig. 2. What is important is that in ceria A, successive CO_2 adsorptions give the same isotherm (a), whereas on ceria B, the first adsorption (b) is marked by a break, the subsequent ones (c) resembling those on ceria A.

The latter facts have already been found on thoria (*5*), and their interpretation is the same: ir study (*1*) shows that CO_2 is chemisorbed according to two different modes, monodentate:
and bidentate:



(monodentate)



(bidentate)

the stabilities of which strongly differ: an evacuation at room temperature suffices to eliminate the latter, whereas the former can be desorbed only at 450°C. On ceria A, carbon dioxide is mainly adsorbed as bidentate, and successive desorption–adsorption cycles give rise to the same volumetric isotherm, and, but for the first adsorption, to the same calorimetric pattern, not exceeding a chemisorption heat value of 35 kcal/mole.

Ceria B behaves differently: the amount of chemisorbed CO_2 is three times larger than on ceria A, and the first amounts are chemisorbed as monodentate, i.e., with a heat larger than 35 kcal/mole (Fig. 1), and a volumetric isotherm branch with a different slope.

B. Oxygen Adsorption

As shown by Fig. 3, oxygen interaction with the ceria B surface consists of two different parts, the first of which is strongly exothermic and corresponds to a total oxygen amount of 3.4 cm^3/g of solid, i.e., to $\Delta x = 0.05$. The difference in x between ceria A and ceria B is about 0.04. Hence the more exothermic part of the oxygen interaction can be interpreted by the oxidation of the solid, according to the equation:

$$CeO_x + \frac{x' - x}{2} O_2 \rightarrow CeO_{x'}$$

the heat of which slowly decreases from 55 kcal/g-atom O for $x = 1.95$ to about 30 kcal/g-atom O when x reaches 2.

Previous study of hypostoichiometric ceria has been made between 600 and 1000°C by Brauer, Gingerich and Holtschmidt (*6*), and between 636 and 1169°C by Bevan and Kordis (*7*). These authors have determined the chemical composition of CeO_x in equilibrium with different pressures of oxygen, and have calculated the partial molar free enthalpy of mixing (or relative partial molar free enthalpy):

$$g_{O_2}{}^M = RT \ln P_{O_2}$$

and the partial molar enthalpy of mixing (or relative partial molar enthalpy):

$$h_{O_2}{}^M = \frac{\partial(g_{O_2}{}^M/T)}{\partial(1/T)},$$

which represents the heat evolved as 1 mole of oxygen is added to an infinite mass of oxide.

According to Bevan and Kordis (*7*) the absolute value of the latter function, at 1080°C, increases from 93 kcal/g-atom O for $x = 1.90$ to 115 kcal/g-atom O for $x = 2.00$. Values of $h_{O_2}{}^{M}$ depend only slightly on temperature. Below 685°C, however, there is a miscibility gap between a fcc phase, the composition of which is close to $CeO_{2.00}$ and a rhombohedral phase, the composition of which is close to $CeO_{1.812}$. If such would be the case in our conditions, the oxidation enthalpy per gram-atom O would be constant whatever x might be.

Our experiments allow us to reach the differential heat per mole of oxygen, which, being measured at a constant volume, differs from the absolute value of $h_{O_2}{}^{M}$ only by a term RT, negligible if it is remembered that the accuracy of heat determinations does not exceed 5%. It can then be deduced from Fig. 3 that our findings contradict those of Bevan and Kordis in three respects:

1. Q varies with x instead of remaining constant as it should if we were in the presence of two distinct phases;
2. Q significantly decreases when x increases;
3. Its value is about half the value reported by the previous authors.

These discrepancies are easily explainable, however, if the different experimental conditions are taken into account. In previous authors' experiments, ceria has been prepared at 800°C, the lowest working temperature was 636°C, and the solid was equilibrated with the gas phase. In our experiments, ceria is prepared at 500°C and is used at temperatures not exceeding 300°C. It is likely that its defect structure is never in true chemical equilibrium with the gaseous phase. Not surprisingly, neither X-ray nor electron diffraction techniques could detect any phase other than CeO_2. Thus, it is deemed likely that the interactions with which we are dealing are purely surface ones and do not concern the bulk of the oxide. Most probably, they consist of the filling up of oxygen vacancies created by the reducing treatment yielding ceria B.

C. Carbon Monoxide Adsorption

Figures 4 and 5 can be interpreted by assuming that CO adsorption is observed as such on ceria B: it is then reversible and implies a maximum heat of 25 kcal/mole. Infrared spectrophotometry establishes that CO is then fixed by the surface oxygen ions of the lattice to give a carboxylate compound (*1*). On ceria A, pure adsorption is at first followed by the reduction of the surface, according to the sequence:

$$CO + * \rightarrow CO_{ads}, \qquad (1a)$$

$$CO_{ads} + O^{2-} \rightarrow CO_2 + \square^{2-}, \qquad (1b)$$

where * designates a CO adsorption site (which actually is an oxygen ion of the surface) and $\square^{2-}$, a charged oxygen vacancy. The reverse of pure adsorption is not to be considered when reaction (1b) immediately consumes the adsorbed CO.

This set of two steps explains the steeply ascending branch (a) of the isotherm in Fig. 5, the residual CO pressure being minute. The total energy involved is the sum of the heats liberated by steps (1a) and (1b), and decreases from the initial value of 52.5 kcal/mole, as shown by Fig. 4. During this process, surface O^{2-} is consumed, so that, after the thirteenth addition, only reaction (1a) is significant: the corresponding break on the calorimetric and volumetric isotherms shows the passage to a regime identical, in both respects, with the features exhibited by ceria B.

D. Adsorption Sequence CO + O₂

Previous discussion shows that the ceria surface can be reduced by CO and reoxidized by oxygen. Thus, alternation of reactions (1a) + (1b) during carbon monoxide admission, and of:

$$O_{2g} + 2\square^{2-} \rightarrow 2O^{2-}, \qquad (2)$$

during oxygen admission, is to be expected. Obviously the oxygen volume required by reaction (2) is half the volume of carbon monoxide which is irreversibly reacted during the sequence (1a) + (1b). Hence the ratio v_2/v_1 found in Table 1. Furthermore, let us call ΔU_1 the heat evolved (at constant volume) during the passage from

1 mole of gaseous CO to 1 mole of adsorbed CO_2 according to the set of reactions (1a) + (1b). Let ΔU_2 be the heat liberated by reaction (2). If we also consider carbon dioxide desorption:

$$CO_{2\,\mathrm{ads}} \rightarrow CO_{2\mathrm{g}} \qquad (3)$$

which implies $-\Delta U_3$ kcal/mole, the total heat of the oxidation process would be:

$$\Delta U = \Delta U_1 + \tfrac{1}{2}\Delta U_2 - \Delta U_3 \simeq -68 \text{ kcal}$$

if reaction (3) is completed, or

$$\Delta U = \Delta U_1 + \tfrac{1}{2}\Delta U_2$$

if CO_2 remains entirely in the adsorbed state. Generally,

$$\Delta U = \Delta U_1 + \tfrac{1}{2}\Delta U_2 - y\Delta U_3,$$

y, comprised between 0 and 1, being the fraction of CO_2 present in the gaseous phase. Finally, therefore:

$$\Delta U = -68 + (1 - y)\Delta U_3 \text{ kcal/mole CO}.$$

Now, in our experiments of successive and alternate adsorptions of carbon monoxide and of oxygen, we assume that the intermediate evacuations do not modify the surface covered by irreversibly adsorbed species. However, it is possible that some CO_2 is spontaneously desorbed during the contacting of the surface with the gases. These amounts increase with the number n of sequences, because of the progressive surface saturation. If then we assimilate the heat,

$$Q_1 + \tfrac{1}{2}Q_2 = Q,$$

during an individual sequence with $-\Delta U$, we must expect:

$$Q - 68 = (1 - y)Q_3.$$

This function decreases with n, as shown in Table 2.

TABLE 2
HEAT EVOLUTION DURING SUCCESSIVE AND ALTERNATE ADSORPTIONS OF CARBON MONOXIDE AND OXYGEN

n	$Q = Q_1 + Q_2/2$	$Q - 68$
1	86	18
2	77	9
3	73	5
4	73	5
5	69	1

E. Reaction CO + $\frac{1}{2}O_2$

The calorimetric pattern exhibited by Fig. 6 shows an evolution of 68 kcal/mole after the second addition of a stoichiometric mixture CO + $\frac{1}{2}O_2$ on ceria A. Hence, formation of surface carbonate only slightly inhibits the major part of catalysis. This is in agreement with the kinetic study (*1*).

The behavior of ceria B is explained if it is remembered that oxidation of this oxide is much faster than its reduction. Therefore, when a stoichiometric mixture is admitted to its surface, oxidation occurs first, with rapid pressure change and heat evolution. Reduction takes place later, and the solid surface slowly recovers its initial oxidation state. Partial oxidations by pure oxygen increase the reduction rate, and therefore allow the time required for the completion of stoichiometric mixture reaction to be reduced. In other words, catalysis is faster on ceria A than on ceria B.

CONCLUSION

Microcalorimetric technique applied to the study of interactions of CO_2 and CO with ceria surfaces gives results which are in agreement with following hypotheses: (i) under our conditions, there is no miscibility gap in the series of nonstoichiometric oxides, so that our catalysts remain single-phased; (ii) the catalytic sequence consists of the set of reactions (1), (2), (3) above, at least in pressure range below 2 Torr. This mechanism has been confirmed and extended to a wider pressure domain by other techniques (*1, 2*).

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