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Catalysis of Carbon Monoxide Oxidation by Cerium Dioxide

I. Correlations between Catalytic Activity and Electrical Conductivity

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A mechanism involving the oxidation and reduction of the solid is presented for carbon monoxide oxidation on cerium dioxide. Expressions for the reaction rate and the electrical conductivity of the catalyst are derived from this mechanism. Experiments have been performed in which these two quantities have been simultaneously recorded. The results agree with the proposed mechanism.

INTRODUCTION

The oxidation of carbon monoxide on cerium dioxide has been incidentally studied by some authors (*1–4*). Rienäcker and coauthors have considered this pure oxide as a limiting case in some series of mixed oxides CeO_2–Al_2O_3 (*1*), CeO_2–ThO_2 (*2*), CeO_2–La_2O_3 (*3*). The activation energy on pure ceria varies from 10 to 16 kcal/mole, possibly because of different preparation modes of the catalyst. No mechanism is given for the catalysis.

We have ourselves studied the oxidation of carbon monoxide on thoria and on cerium-doped thoria (*5*), and concluded that the oxidation and reduction of the solid played a role which was nil in the former case and very limited in the latter (*6*). It was therefore of interest to see whether this oxidation and reduction of the solid occurred in the case of pure ceria. Such a mechanism has already been put forward in the case of uranium–thorium mixed oxides (*7*).

Previous studies of the interaction of the gases CO, O_2, and CO_2 with ceria were performed in our laboratory and involved several techniques: gravimetry, microcalorimetry, electrical conductivity measurements, and infrared spectrophotometry. The main results can be summarized as follows: CO_2 gives rise to an adsorption which is not always reversible, but in which its chemical entity is maintained; on the contrary, CO adsorption is always accompanied by a reduction of the initial solid, the composition of which passes from $CeO_{1.985}$ to $CeO_{1.945}$ at 300°C. Simultaneously, CO is transformed into CO_2. The initial *n*-type conductivity of the oxide increases during this treatment.

Oxygen adsorption is weak on the initial solid, but very rapid at all temperatures on the reduced one, the conductivity of which diminishes during the oxidation.

Accordingly, the following mechanism can be tentatively given for the catalysis of carbon monoxide oxidation:

$$\text{(I)}\qquad CO_{gas} \rightleftarrows CO_{ads};$$

$$\text{(II)}\qquad CO_{ads} + O_{\square}^{2-} \rightarrow CO_{2\,ads} + \square^{2-};$$

$$\text{(III)}\qquad CO_{2\,ads} \rightleftarrows CO_{2\,gas};$$

$$\text{(IV)}\qquad O_{2\,gas} + 2\,\square^{2-} \rightarrow 2\,O_{\square}^{2-},$$

where $\square$ designates a vacancy in the anionic sublattice of CeO_2.

Such a mechanism, involving alternating reduction and oxidation of the catalyst surface, has been put forward in some other instances, e.g., the oxidation of carbon monoxide on CuO (*8*), or of hydrogen on ferric oxide (*9*). Our purpose, in the present work, is to check the consistency of the above mechanism by simultaneous measurements of the catalytic activity and the electrical conductivity of ceria.

Experimental Methods

Reactants and Catalyst

All the gases used contained less than 50 ppm impurities. Cerium dioxide was prepared by thermal decomposition in air of $(NH_4)_2\ Ce(NO_3)_6$ at 500°C during 24 hr. The residue was then treated by an argon flow (5 liters/hr) at 450°C during 16 hr. Its composition then corresponded to $CeO_{1.985(\pm 0.003)}$, as determined by chemical analysis. Its surface area was $27(\pm 2)\,m^2/g$.

Many samples answering these characteristics have been used in this investigation. Results summarized below deal with their mean behavior. Numerical values concerning a particular sample will be given for illustration.

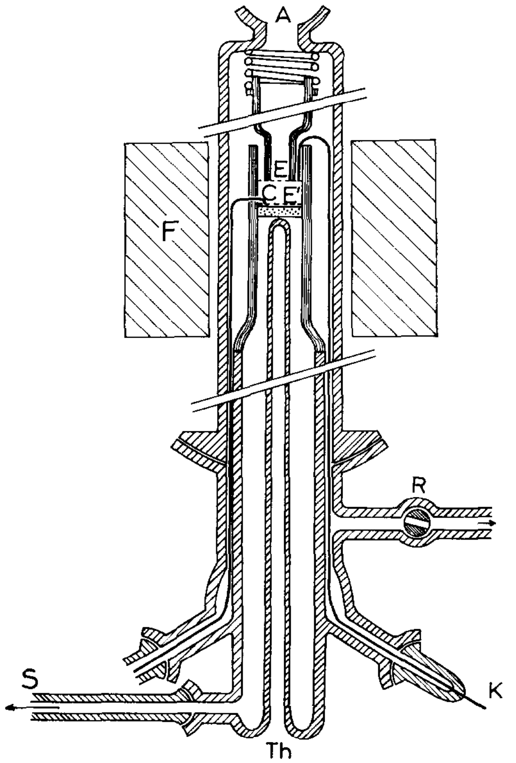

FIG. 1. Reactor allowing simultaneous measurement of catalytic activity and of electrical resistance. A: gas inlet; C: catalyst; E-E': electrodes; F: furnace; K: kovar passage; R: stopcock for reactor purging; S: gas outlet; Th: thermocouple well; ▨ : Pyrex; ☰ : quartz; ▦: glass-sinter; — stainless steel.

Apparatus for the Study of Catalysis Kinetics (Fig. 1)

This basically consisted of a differential flow reactor, where the fractional conversion was less than 1%. The amount of carbon dioxide in the effluent was continuously analyzed by ir spectrophotometry. The originality of the reactor design is that it allowed simultaneous measurements of the electrical resistance of the catalyst and its activity. The powder was enclosed between stainless-steel grids which presented to the gas a free area equal to 34% of the total area. These grids were connected to a dc bridge, which was liable to an error of 1% up to $10^{11}\,\Omega$ and of 2–3% up to $10^{13}\,\Omega$. The electrical resistance of the empty quartz cell was much greater ($5 \times 10^{10}\,\Omega$ at 340°C) than the resistance of a typical catalyst ($7 \times 10^8\,\Omega$ at 340°C). Likewise, it was checked that an empty cell had no catalytic activity.

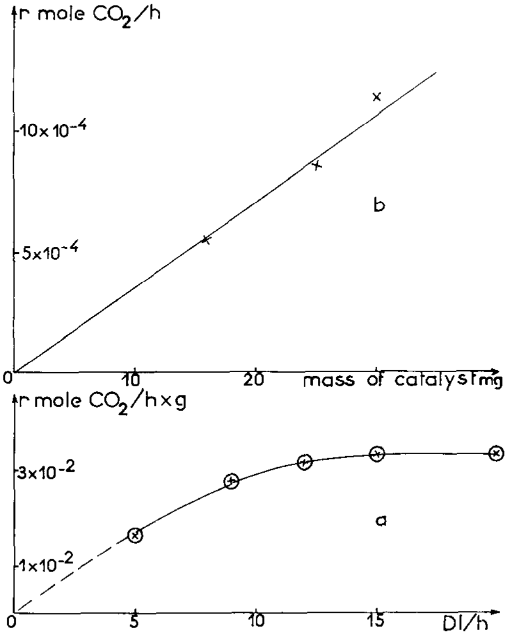

FIG. 2. Tests on the influence of diffusion at 322°C, $P_{O_2} = P_{CO} = 253$ Torr: (a) specific activity vs flow rate (mass of catalyst: 16 mg); (b) activity vs catalyst mass (flow rate: 15 l/h).

Diffusion effects have been studied. Fig. 2a shows that external diffusion can be avoided if the gaseous flow rate is equal to or greater than 15 liters/hr. Fig. 2b shows that extragranular internal diffusion is avoided if a catalyst mass less than 30 mg is used. These conditions were fulfilled in all the experiments subsequently reported.

For a typical run, the reaction rate r measured with this reactor was 3.5×10^{-2} moles CO_2 per hr and per g, at 322°C, under partial pressures $P_{O_2} = P_{CO} = 253$ Torr, whereas in a conventional batch reactor the initial rate was found, under the same conditions, to be $r = 5.5 \times 10^{-2}$ moles CO_2/h g. Taking into account the very different set-ups, the agreement between these two values may be considered as acceptable.

Fig. 3 gives an example of the simultaneous recordings obtained for the catalytic activity (curve a) and for the electrical resistance (curve b). As usual in experiments made on finely divided solids, the electrical conductivity data have no absolute value. However, their relative variations are valuable, especially when they can be directly compared to simultaneous changes of catalytic activity.

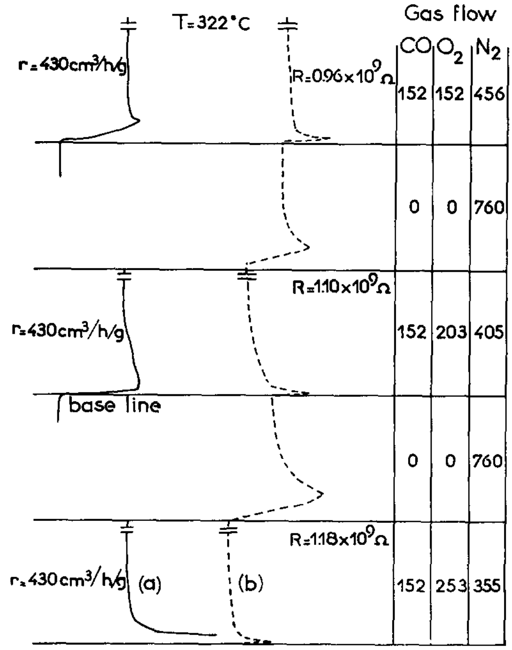

FIG. 3. Experimental recording of: —— (a) ir analyzer; ---- (b) resistance measurement apparatus. Gaseous flow composition (partial pressures in Torr) are indicated at the right.

EXPERIMENTAL RESULTS AND INTERPRETATION

Catalysis Kinetics

Order with respect to oxygen. At a given temperature the reaction rate remained constant when, for a given carbon monoxide partial pressure, the oxygen partial pressure P_{O_2} was varied from 200 to 400 Torr. Therefore, the partial order with respect to oxygen is zero (Fig. 4a).

Order with respect to carbon monoxide. At a given temperature, for a given oxygen partial pressure, the carbon monoxide partial pressure P_{CO} was varied from 25 to 250 Torr. The points representing log r as a function of log P_{CO} fitted a straight line, the slope of which was close to 0.84 (±0.06), which is then the partial order with respect to carbon monoxide (Fig. 5a).

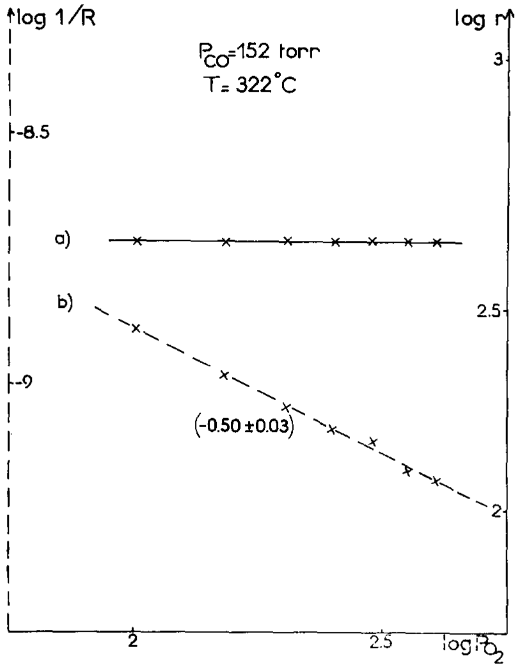

FIG. 4. Simultaneous measurements of catalytic activity —, and of electrical resistance ----, vs oxygen partial pressure.

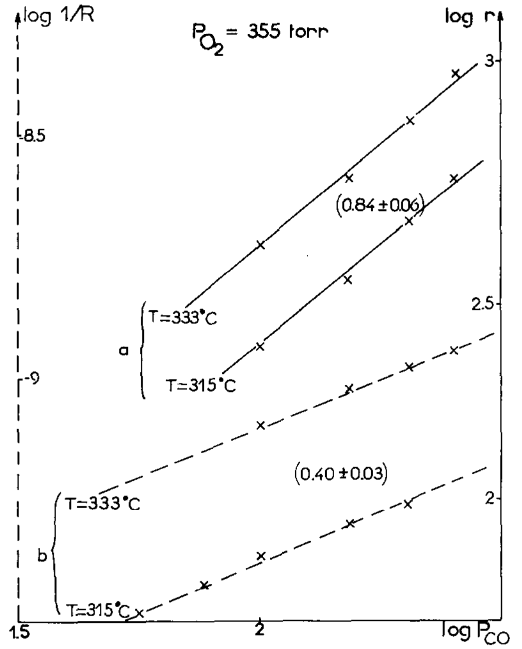

FIG. 5. Simultaneous measurements of catalytic activity —, and of electrical resistance ----, vs CO partial pressure.

Activation energy. When for different compositions of the reactant mixtures, log r was plotted vs $1/T$, nearly parallel straight lines were obtained, the slopes of which corresponded to an activation energy of 20 (±1) kcal mole^{-1} (Fig. 6a).

Inhibiting influence of carbon dioxide. Introducing a very low amount of carbon dioxide in the reactant mixture ($P_{CO_2} = 10^{-3} P_{O_2}$) depressed the catalytic activity. This decrease remained constant when higher contents of carbon dioxide were used, which proves that minute amounts of this gas are enough to create surface poisoning, which remains slight even for higher amounts.

In the following, only reacting mixtures of carbon monoxide and oxygen will be considered.

Electrical Conductivity Measurements

In all our experiments, ceria exhibited n-type semiconductivity behavior.

Variation of the electrical resistance R with P_{O_2}. In the conditions where the zeroth order with respect to oxygen was found, the simultaneous measurement of R showed that log $1/R$ was a linear function of log P_{O_2}, the slope of the straight line being close to −0, 50 ± 0.03 (Fig. 4b).

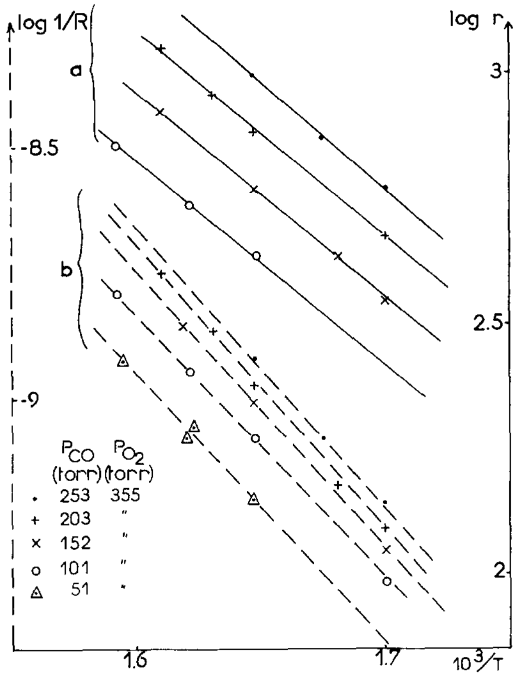

FIG. 6. Simultaneous measurements of catalytic activity —, and of electrical resistance ----, for different reactant mixtures, vs $1/T$.

Variation with P_{CO}. In the conditions where the order 0.84 with respect to carbon monoxide was found, the simultaneous measurement of the resistance showed that log $1/R$ was a linear function of log P_{CO}. The slope of the straight line was very close to 0.40 ± 0.03 (Fig. 5b).

Temperature variation of conductivity. With different reactant mixtures, the conductivity varied and so did catalytic activity. But the variations of log $1/R$ vs $1/T$ for different gaseous compositions gave parallel straight lines the slopes of which corresponded to an activation energy of 25 (±1) kcal mole^{-1} (Fig. 6b).

If the reactor was purged with N_2 in the course of an experiment, in order that the steady state reached by the catalyst during catalysis at the working temperature could be maintained, and if conductivity measurements were then performed under a nitrogen flow, the conduction activation energy was 14 ± 1 kcal/mole.

Interpretation

If we consider again the mechanism already given for the catalytic action of ceria in carbon monoxide oxidation and designate by r_i the rate of the ith step, the catalysis rate is:

$$r = r_2, \tag{1}$$

and the steady-state hypothesis for the vacancies $\square^{2-}$ enables us to write:

$$r_2 = 2r_4; \tag{2}$$

or

$$k_2(\mathrm{CO})_{\mathrm{ads}}(\mathrm{O}^{2-}_{\square}) = 2k_4P_{\mathrm{O}_2}(\square^{2-})^2. \tag{3}$$

From the preceding kinetic results,

$$r = r_2 = kP_{\mathrm{CO}}^{0.84}. \tag{4}$$

Therefore, we may conclude that $(\mathrm{CO})_{\mathrm{ads}}$ varies as $P_{\mathrm{CO}}^{0.84}$ and that $(\mathrm{O}^{2-}_{\square})$ does not appreciably change with the partial pressures of the reactants, and thus can be considered as constant during catalysis.

Therefore,

$$(\square^{2-})^2 = kP_{\mathrm{CO}}^{0.84}/(2k_4P_{\mathrm{O}_2}) \tag{5}$$

Let us at present assume that the conduction electrons, which are the majority carriers, come from the ionization of anionic vacancies. The electrical conductivity can be written:

$$\sigma = b(\square^{2-})\exp(-E_c/RT), \tag{6}$$

E_c being the conduction activation energy at a constant concentration of $\square^{2-}$. Therefore, replacing $(\square^{2-})$ by the above expression,

$$\sigma = cP_{\mathrm{CO}}^{0.42}\mathrm{PO}_2^{-0.5}\exp\left(\frac{-\dfrac{E_2}{2} + \dfrac{E_4}{2} - E_c}{RT}\right) \tag{7}$$

This agrees with our experimental findings. Firstly, σ varies as $P_{\mathrm{CO}}^{0.42}$ and as $P_{\mathrm{O}_2}^{-0.5}$. Secondly, $E_c = 14$ (±1) kcal mole^{-1}, $E_2 =$ 20 (±1) kcal mole^{-1}, and E_4, the activation energy for the ceria reoxidation, is probably very low, as stated before. Hence,

$$E_2/2 - E_4/2 + E_c = 24\ (\pm1.5)\ \text{kcal mole}^{-1},$$

whereas the value derived from direct measurements is 25 (±1) kcal mole^{-1}.

DISCUSSION

As is well known, the mere fact of checking final equations derived from a hypothetical mechanism does not constitute by itself a proof of its validity. A first objection to our mechanism is that we have postulated $E_4 = 0$, without any direct proof of this value. But, as already stated, the reoxidation of ceria is so rapid in our working temperature range that a low value of E_4 is most likely. A second objection could be that the adsorbed species in our mechanism bear no electrical charge. Although it could well happen that they do bear a charge, it does not seem to us that developing the corresponding scheme is worth the complication. Indeed, our experiments prove that the variations of conductivity due to polarization of the various adsorbates are much smaller than the variations due to the oxidation and reduction of the solid. Let us remark at that stage that Eq. (6), giving the electrical conductivity of the oxide, is consistant both with a band model and with an activated mobility ("hopping" type) mechanism, which seems to be more likely (*10*).

A third objection is that we are resorting to a defect model of ceria which involves anionic vacancies, whereas recent investigations (*11, 12*) conclude that the nonstoichiometric defect structure of ceria can most likely be interpreted in terms of ionized cerium interstitials. However, this objection does not seem to rule out the validity of the proposed mechanism, firstly because the quoted investigations deal with a higher temperature range than ours, and secondly because we have checked the occurrence of the reduction (II) of the solid by CO in our case. Thus, the extraction of oxygen from the solid seems the only possibility of passing from CO to $\mathrm{CO_2}$.

A simultaneous measurement of catalytic activity and of electrical conductivity in conditions where the latter has a physical meaning would be desirable. This kind of experiment would call for the use of single crystals and has already been carried out on Cu_2O by Wise and coworkers (*13*). Although this ultimate goal has not yet been reached in our case, it seems to us that a quantitative correlation of the type found between catalytic activity and a physical property measured in the same conditions can give a firm foundation for the postulated mechanism.

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