Catalytic Carbon Monoxide Oxidation on X-Irradiated Alumina

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The catalytic oxidation of carbon monoxide in the presence of alumina has been studied in a flow system over the temperature range 25° to 400°C. In the course of the reaction, the catalyst has been submitted to irradiation with X-rays (55 kV) at a dose rate of 2×10^{19} eV g^{-1} h^{-1}. Comparison of the results obtained under similar conditions with and without irradiation, indicates that, at a temperature below 300°C, the catalytic activity of irradiated alumina is much higher. This fact may be related to the very important lowering of the activation energy under irradiation: 18 kcal for the unirradiated catalyst, about 0 kcal in the temperature range 80–300°C and about 4 kcal at lower temperature for the irradiated one.

Nevertheless the reaction order under irradiation remains the same as for un-irradiated catalysts: it approaches unity with respect to CO pressure, and is comprised between one-fifth and one-half with respect to O_2 pressure.

These results as well as previous ones related to the sorption of CO, O_2, and CO_2 on alumina submitted to irradiation lead to the conclusion that the rate-determining step for the catalytic oxidation of CO on Al_2O_3 is the chemisorption of O_2. This step is accelerated to a considerable extent by the irradiation of alumina.

1. INTRODUCTION

In the last few years, much experimental work has been devoted to the study of the influence of irradiation—by photons (UV, X-, and γ-rays) as well as by particles (neutrons, electrons, and heavy charged particles)—on the adsorptive and catalytic properties of solids. A few review papers have already been published on this subject (*1, 2, 3*).

Nevertheless, most experiments in this field are concerned with the modifications of properties induced through irradiation of the solid prior to the study of the adsorption or of the catalytic reaction. The observed new properties are usually related either to the created lattice defects, or to the excess free carriers produced by irradiation and subsequently trapped in the solid. Numerous factors exert an influence both on the nature and the importance of the induced modifications. Among them we cite the nature, the intensity, and the total dose of radiation, and also the temperature at which the solid has been irradiated, the time elapsed between irradiation and subsequent utilization in a catalytic reaction, and the impurity content of the solid. As a consequence the interpretation of the results from a catalytic point of view frequently becomes very intricate.

On the other hand, the study of the modifications induced in the course of irradiation seems very promising as regards the understanding of catalytic processes. This is especially true for radiation producing few lattice defects such as medium energy photons. This has been put in evidence in recent theoretical (*4, 5, 6*) and experimental studies (*7–12*).

In connection with this problem, the investigation of the effect of radiation on the catalytic CO oxidation has been undertaken. This very simple reaction indeed

has been extensively studied and its theoretical features are clearly understood.

This study is carried out with alumina as a catalyst. In our laboratory, indeed, numerous experimental results have recently been obtained using this solid, concerning the radiative sorption of CO, CO_2, and O_2 (8, 9) as well as the radiolysis of adsorbed CO_2 (13).

The low reproducibility of measurements made by other workers (12) as well as our own results on the adsorption of different gases induced by irradiation of solids, indicate that a stationary value of the activity of irradiated catalysts is only attained after a relatively long period of time. For this reason, a flow system has been used for the measurement of reaction rate. Irradiation has been carried out with X-rays (55 kV). In this energy range, indeed, the production of lattice defects may be neglected, but, in contrast with UV radiation used by several workers, the X energy absorbed by the catalyst is rather evenly distributed in the solid.

2. EXPERIMENTAL

Catalyst. The alumina quality "basique pour chromatographie" supplied by Carlo ERBA has been submitted to the treatment
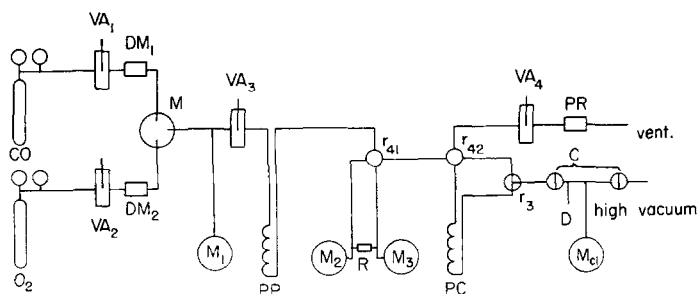
tended X-ray irradiation (up to doses of 10^{23} eV g^{-1}) in a CO_2 atmosphere.

Apparatus and technique. The apparatus used for the measurement of the reaction rate is described by Fig. 1. The reaction gases CO and O_2 are supplied from cylinders. The flow rate is adjusted by needle valves (VA_1 and VA_2) and measured by differential oil manometers (DM_1 and DM_2); the upstream pressure, nearly 760 torr, is controlled by the manometer M_1. The gases, mixed in M, and purified in trap PP at liquid oxygen temperature, flow on the catalyst contained in reactor R, which may be bypassed with the four-way valve r_{41}, then traverse trap PC at liquid oxygen temperature, where CO_2 is collected. The total pressure in the reactor and in the trap PC is maintained below 400 torr in order to avoid CO condensation in the traps. This is realized with the vacuum pump PR, the pressure being adjusted with needle valves VA_3 and VA_4 and measured with manometer M_2 and M_3.

The collection trap PC may be bypassed by the four-way valve r_{42} and connected either with a vacuum line or with a calibrated volume C comprising a MacLeod gauge and a cold finger at liquid nitrogen temperature.

FIG. 1. Apparatus for CO catalytic oxidation: PP, purification trap; PC, CO_2 collection trap; VA, needle valve; Mcl, MacLeod gauge; D, cold finger; C, calibrated volume; PR, vacuum pump; M, manometers; r3–r4, 3- or 4-way valves; DM, flow meters.

described in previous studies (8): heating at 1.030°C for 70 hr. The crystalline form is mainly "Kappa," with remaining traces of "Alpha." The specific surface area, as obtained by the BET method using nitrogen adsorption, is 25 m^2 g^{-1}. This value of the surface area remains unaltered after ex-

The reactor is a Pyrex tube, of 6-mm internal diameter, in which about 5 g of powdered catalyst is packed and maintained between pressed Pyrex wool. It is immersed in a thermostated oven which can be heated up to 450°C. The oven is provided with a thin mica foil allowing for X-

ray penetration. It is surrounded by a lead shielding supplied with an irradiation window in which the X-ray tube is embedded, and with staggered apertures for Pyrex tubes and electrical connections.

Procedure. When all the experimental parameters (temperature, pressure, flow rate ...) have attained stationary values, the trap PC is cooled in liquid oxygen, the gaseous flow is deflected in PC by rapidly turning the valve r_{42} and CO_2 is allowed to condense. After a certain definite time, excess of CO and O_2 is pumped off, CO_2 is distilled in the cold finger of volume C, and after decondensation, CO_2 pressure is measured with the MacLeod gauge. With the usual flow rate between 50 and 100 cc min^{-1}, the duration of the condensation was about 10 min.

The complete operation is repeated until reproducible results are obtained.

Irradiation. Irradiation is carried out with an X-ray tube Machlett OEG 60. Usual working conditions are 55 kV, 25 mA. The distance between the reactor and the focus of the X-ray tube is about 10 cm. The absorbed dose under these conditions is 6 $\times 10^{15}$ eV sec^{-1} per gram of solid. This value is proportional to the current. It has been obtained by chemical dosimetry with ferrous sulfate and by calorimetric measurements (14). This is a mean value, as the absorbed dose varies by about a factor of 2 between the extreme sides of the solid sample.

Reagents. Cylinder CO (quality N40 supplied by L'Air Liquide) contains less than 500 ppm of impurities, mainly CO_2, H_2O, and light hydrocarbons. The impurity content of cylinder O_2 (quality A40 supplied by L'Air Liquide) is less than 100 ppm. After purification in the cold trap PP of the reaction apparatus, concentration of condensable impurities in the flowing mixture is less than 5 ppm.

3. RESULTS

3.1. General

After a series of preliminary measurements, the following conclusions have been drawn:

(1) Without catalyst, the quantity of carbon dioxide formed in the reactor at a temperature of 400°C and for a residence time of 1 min, is lower than the content of condensable impurities ($\cong 5$ ppm) in the reagents. This fact has been verified respectively with and without irradiation of the reacting mixture.

(2) The quantity of CO_2 condensed in the trap PC is proportional to the duration of the condensation and does not depend on the flow rate, within the limits 30 to 85 cc TPN min^{-1}, that correspond, under our usual working conditions ($20° < T < 350°C$, 5 g of catalyst, $P \sim 375$ torr) to residence times between 0.6 and 3 sec. That means that the degree of conversion, as calculated from the quantity of CO_2 condensed, is proportional to the residence time and that the quantity of CO_2 produced is only a function of catalyst temperature, P_{O_2}, P_{CO}, and irradiation. It follows that, at the low conversions observed in this work, the produced CO_2 does not exert any inhibitory effect on the reaction.

(3) The measured reaction rates are proportional to the weight of catalyst and quite reproducible from sample to sample. For this reason all the results in the following will be reduced to 1 g of catalyst.

(4) All results obtained with a given sample of alumina, are quite reproducible and do not depend upon the "history" of the catalyst. But every modification of an experimental parameter (temperature, partial pressure of reagents, irradiation, ...) results in a slow evolution of the catalytic activity to the stationary value corresponding to the new conditions. This stationary value of the reaction rate is usually obtained after 30 to 60 mins of contact between the catalyst and the gaseous flow.

(5) No correction of the results for volume variations in the course of the reaction are necessary, maximum conversion being always less than 0.7%.

3.2. Results on Unirradiated Catalyst

Under the usual working conditions ($P = 370$ torr, $P_{CO}/P_{O_2} \cong 2$, flow rate $\cong 50$ cc min^{-1}, 5 g catalyst) conversion can only be detected at temperatures above 180°C.

The results of the measurements made from 210° to 360°C are shown on the Arrhenius plot of Fig. 2. The values of the
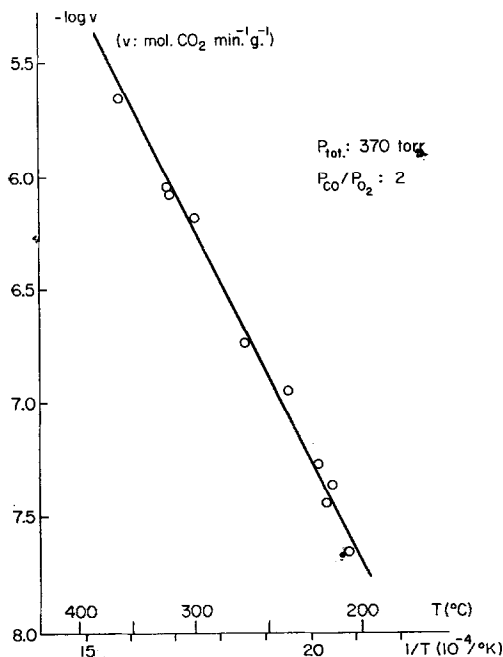

FIG. 2. Catalytic oxidation of CO on alumina. Temperature influence.

activation energies and of the pre-exponential factor deduced from the figure amount, respectively, to 18 ± 2 kcal and 1.6×10^{-2} moles CO_2 torr^{-1} g^{-1} min^{-1}.

O_2 pressure maintained at 120 torr. Pressure variations of O_2 remain between 30 and 120, with a constant CO pressure fixed at 260 torr. Results shown in Figs. 3 and 4 indicate that the order with respect to CO is close to 1, whereas the order with respect to O_2 is one-half at 220°C, and one-fifth at 325°C.

3.3. Results under Irradiation

Influence of temperature. With the same working conditions, X-ray irradiation (55 kV, 25 mA) of the catalyst in contact with the flowing mixture of the reagents gives rise to easily measurable conversion at room temperature. At this temperature the reaction rate corresponds to the one measured at 260°C without irradiation.

The measurements of the reaction rate from 20° to 365°C are expressed by the Arrhenius plot shown in Fig. 5. On the same figure, the straight Arrhenius line of Fig. 2 corresponding to the unirradiated catalyst is shown for comparison.

Three domains can be distinguished on the curve of Fig. 5:

(a) At low temperature ($T < 50°C$), the activation energy is positive, but small. The value, imprecise because of the low measured conversion, is in any case smaller than 6 kcal.

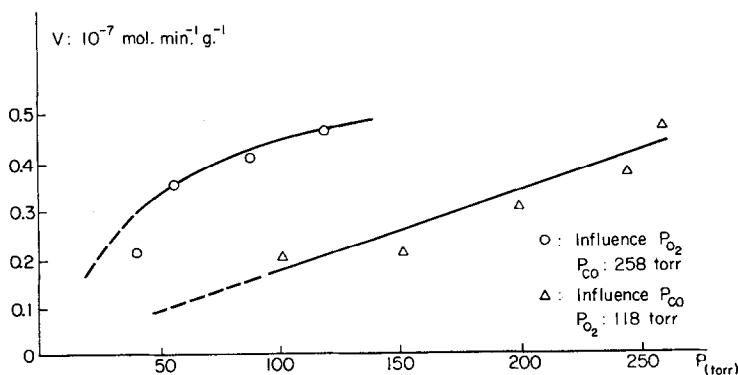(b) From 50° to 300°C, the reaction rate

FIG. 3. Catalytic oxidation of CO on alumina. Influence of the partial pressure of the reagents at 220°C.

The order of the reaction with respect to the partial pressure of CO and O_2 is determined at 220° and 325°C. CO pressure is allowed to vary from 70 to 300 torr, with

does not depend upon the temperature; its value is the same as that measured at 300°C on unirradiated catalyst.

(c) At higher temperatures the activation

energy is about the same for unirradiated and irradiated catalyst.

One may conclude that the irradiation markedly increases the catalytic activity of alumina by a factor reaching 10^6 at room temperature and 10^2 at 200°C.

results, as expressed by Figs. 6 and 7, lead to following conclusions:

The order with respect to CO pressure is not affected by irradiation and is close to unity at both temperatures.
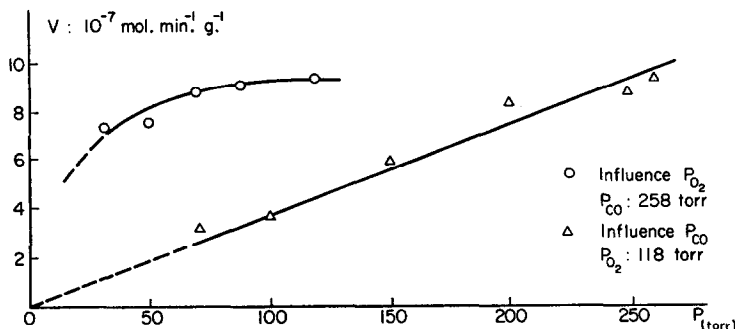
Values of the reaction order with respect

FIG. 4. Catalytic oxidation of CO on alumina. Influence of the partial pressure of the reagents at 325°C.

It is important to note here that, when stopping the irradiation, the "thermal" value of the reaction rate is restored after less than 10 min (minimum duration of a measurement). Post-radiation catalytic effects, if any, are therefore very short, even at room temperature.

to O_2 pressure result varying from one-eighth at 100°C to one-third at 350°C. Let us recall that, without irradiation, the order was between one-fifth and one-half, depending upon the temperature. If moreover we take into account the fact that the range of temperature where the reaction is
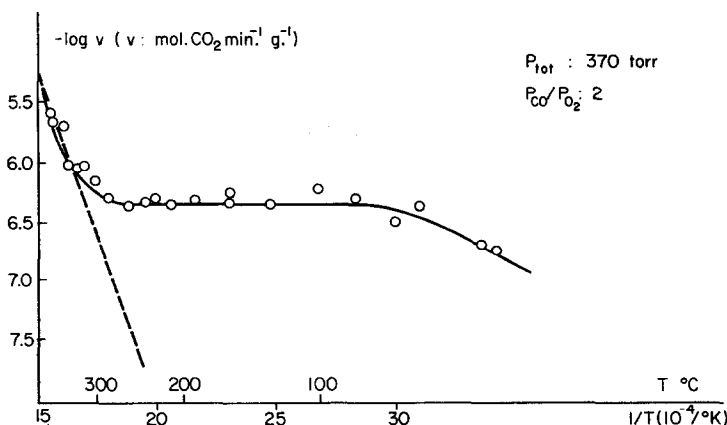

FIG. 5. Catalytic oxidation of CO on X-irradiated alumina. Temperature influence.

Influence of the partial pressure of the reagents. The reaction rates under irradiation at 55 kV, 25 mA are measured at 100° and 350°C, either with constant CO pressure of about 250 torr, as a function of O_2 pressure, or with constant O_2 pressure of 120 torr, with varying CO pressure. The

studied is somewhat different with and without irradiation, we may conclude that the order with respect to O_2 is very slightly affected by irradiation.

Influence of irradiation intensity. The influence of the intensity of irradiation is investigated at 25° and 100°C with the
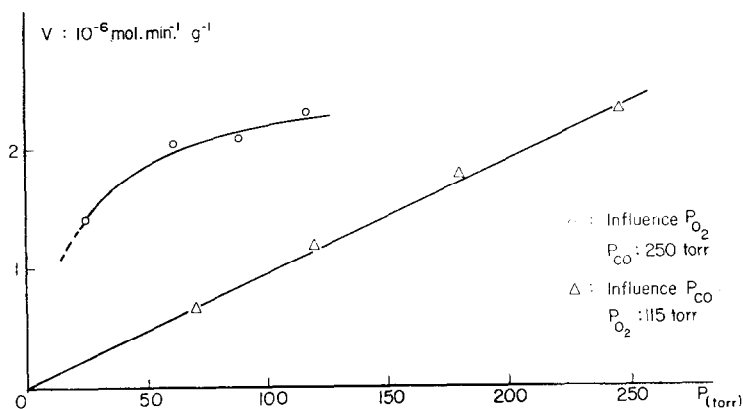
Fig. 6. Catalytic oxidation of CO on X-irradiated alumina. Influence of the partial pressure of the reagents at 350°C.
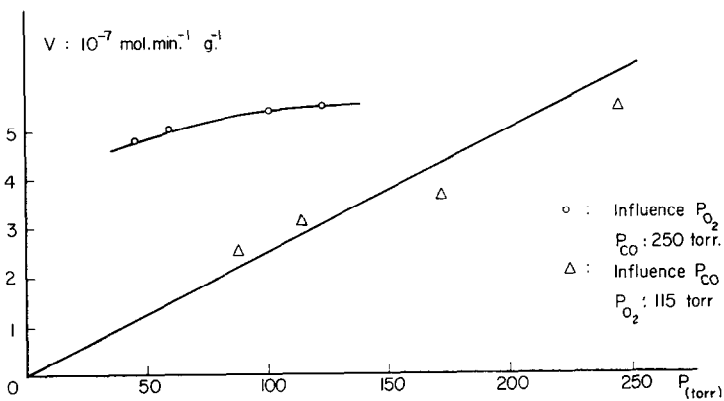

Fig. 7. Catalytic oxidation of CO on X-irradiated alumina. Influence of the partial pressure of the reagents at 100°C.
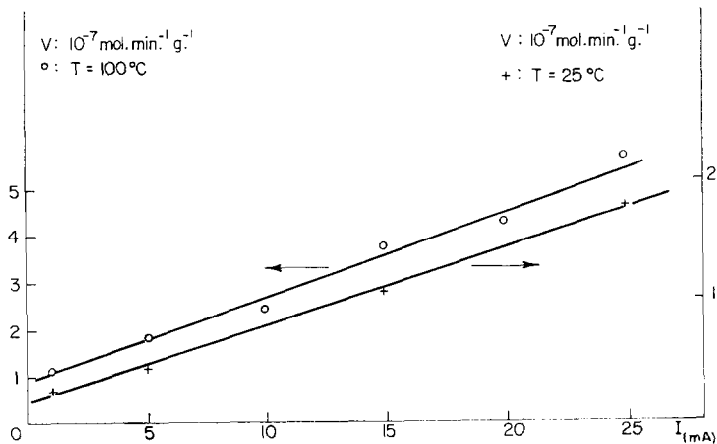

Fig. 8. Catalytic oxidation of CO on X-irradiated alumina. Influence of the radiation intensity.

stoichiometric mixture at a flow rate of 50 cc min⁻¹ and a pressure of 370 torr.

Results are those of Fig. 8 showing a plot of reaction rate versus intensity of irradiation as expressed in mA of electron current in the X-ray tube. Let us recall that 1 mA corresponds to an absorbed energy of $2.4 \ 10^{14}$ eV g⁻¹ sec⁻¹ (cf. Section 2). It must also be noted that at both temperatures considered, without irradiation, the conversion is not measurable and consequently the reaction rate is approximately zero at zero intensity. In both cases, the relationship between reaction rate and intensity is linear, but not passing through the origin, for $I > 1$ mA. But a bend must exist at lower intensity.

The chemical radiation yield G is calculated with respect to the radiation energy absorbed by the solid, since the energy adsorbed in the reagent is negligible and does not give rise to measurable conversion in the absence of catalyst. It is clear from Fig. 8 that G depends on the intensity and the temperature. The following values are obtained:

at 25°C: $G \cong 27$ $(I > 1$ mA$)$
$G > 80$ $(I < 1$ mA$)$

at 100°C: $G \cong 75$ $(I > 1$ mA$)$
$G > 440$ $(I < 1$ mA$)$

4. COMPLEMENTARY RESULTS

We here recall several results of previous studies $(8, 9)$. The adsorption of CO, O_2, and CO_2 has been investigated on irradiated alumina and results of this study have been reported in two recent papers. As an introduction to the following discussion, we summarize here the principal conclusions of these studies.

For the case of CO and O_2, the following facts must be pointed out:

Irradiation induces a complementary adsorption of CO and O_2 in the whole temperature range studied (20° to 300°C). This adsorption is not reversible: it means that, when stopping the irradiation, no desorption of gas results.

The observed values of the adsorption rate are 5×10^{16} molecules g⁻¹ min⁻¹ for oxygen and 1.5×10^{16} molecules g⁻¹ min⁻¹ for CO at a pressure of 100 torr and an irradiation intensity of 25 mA at 55 kV. These values are proportional to the irradiation intensity and the gas pressure. Let us note that the gas–alumina system is submitted to irradiation only when adsorption equilibrium is reached. The preceding values therefore concern a pure radioadsorption phenomenon.

After long irradiation, of about 10 hr at 25 mA, an adsorption equilibrium is attained for the case of O_2. The coverage fraction at the equilibrium under irradiation is about ten times the value corresponding to thermal equilibrium. Under the same conditions, adsorption equilibrium for CO was not obtained after 80 hr of irradiation.

At room temperature, if the irradiation is stopped before the adsorption equilibrium under irradiation is attained, adsorption is still observed, with regularly decreasing rate, for more than 10 hrs.

For the case of CO_2 all the measurements under irradiation were carried out at the same pressure of 0.4 torr with the temperature varying from 20° to 345°C. The value of 0.4 torr corresponds approximately to the partial pressure of CO_2 in the gaseous mixture leaving the reactor in most of the experiments described in Section 3. The initial adsorption or desorption rates observed when the irradiation is applied to the CO_2-alumina system
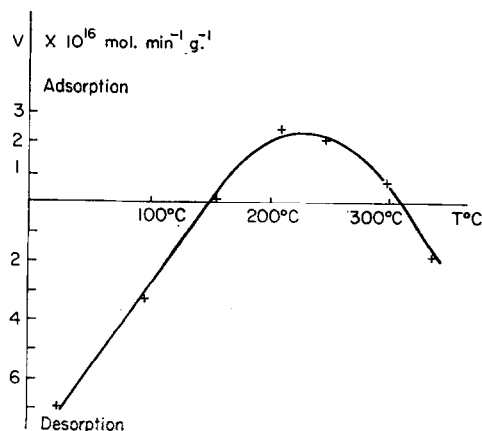

FIG. 9. Sorption rate of CO_2 on X-irradiated alumina (55 kV, 25 mA).

at the adsorption equilibrium, are represented in Fig. 9. Three temperature ranges can be distinguished:

(a) at low temperature $(T < 150°C)$ irradiation causes CO_2 desorption; thermal adsorption equilibrium however is rapidly restored upon stopping irradiation;

(b) for T ranging from 150° to 310°C, complementary adsorption is observed which is not reversible;

(c) for $150° < T < 310°C$, reversible desorption is again observed.

The isosteric heat of adsorption of CO_2 was also determined from adsorption isotherms. Its low-temperature value $(T < 220°C)$ is about 2-3 kcal, but in the high-temperature region, this value is higher than 10 kcal. It follows that a transformation from loosely bound to chemisorbed CO_2 takes place at about 220°C.

5. DISCUSSION

The most striking result of this work is the considerable enhancement of catalytic activity obtained through irradiation of alumina at a rather low intensity. The same value of the reaction rate was obtained on unirradiated alumina at 210°C and, at 25°C, on the same solid submitted to the low X intensity of 1 mA at 55 kV (corresponding to an absorbed energy of 2.4×10^{14} eV sec^{-1} g^{-1}).
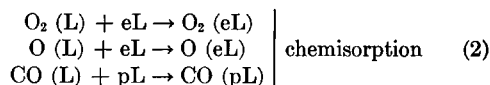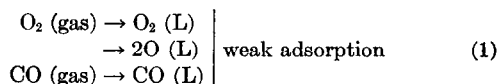
Comparison of our results with those of Schwab (10) and co-workers for the same reaction in presence of ZnO submitted to UV radiation points to an interesting fact. Very similar values of the activation energies and of the order of the reaction with respect to reactive gases, were obtained in both cases as well as very similar forms of the Arrhenius plots. Thus it seems that, from a catalytic point of view, high-energy radiation produces in solids effects which are qualitatively similar to those generated by low-energy photons whose frequency generally corresponds to adsorption bands in the solid and which therefore should be much more selective. Quantitative correlation is, however, not possible because values of the absorbed energy were not cited in Schwab's paper.

The remainder of this discussion is devoted to the mechanism of the catalytic reaction and we will try to show that the irradiation of the catalyst may throw light upon this mechanism.
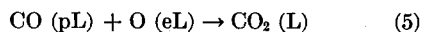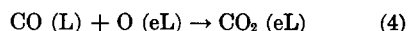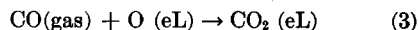
Quite generally, every catalytic reaction may be divided into three principal steps or groups of steps: one or several adsorption steps; one or several reaction steps; one or several desorption steps.

Adsorption steps, according to the electron theory of adsorption and catalysis, involve the following: formation of a weak bond between gaseous molecules and the surface, possibly including a dissociation of these molecules; transformation of this weak adsorption into chemisorption through capture of a free carrier of the solid by the adsorbed molecule.

It is generally accepted that chemisorbed species are necessary for catalytic reactions to take place. In the case considered here, the adsorption steps may be written, using symbol (L) for a weak adsorption and eL and pL for a free electron and a free hole, respectively,

$$\left. \begin{array}{l} O_2 \text{ (gas)} \rightarrow O_2 \text{ (L)} \\ \qquad\quad \rightarrow 2O \text{ (L)} \\ CO \text{ (gas)} \rightarrow CO \text{ (L)} \end{array} \right| \text{weak adsorption} \qquad (1)$$

$$\left. \begin{array}{l} O_2 \text{ (L)} + eL \rightarrow O_2 \text{ (eL)} \\ O \text{ (L)} + eL \rightarrow O \text{ (eL)} \\ CO \text{ (L)} + pL \rightarrow CO \text{ (pL)} \end{array} \right| \text{chemisorption} \qquad (2)$$

Reaction steps take place either between a chemisorbed molecule and a gaseous reactant, or between two adsorbed molecules, one of them at least being chemisorbed. The latter case probably involves the migration of an adsorbed molecule on the surface of the solid. Indeed, over the temperature range considered here, the coverage fraction of the surface is very low and in this case, the probability of finding two adjacent chemisorbed species is negligible. Examples are

$$CO\text{(gas)} + O \text{ (eL)} \rightarrow CO_2 \text{ (eL)} \qquad (3)$$

$$CO \text{ (L)} + O \text{ (eL)} \rightarrow CO_2 \text{ (eL)} \qquad (4)$$

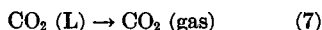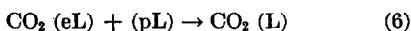$$CO \text{ (pL)} + O \text{ (eL)} \rightarrow CO_2 \text{ (L)} \qquad (5)$$

Desorption requires disruption of the weak adsorption bond. Sometimes, however,

a change of chemisorption into weak adsorption is needed also.

These steps are

$$CO_2 (eL) + (pL) \rightarrow CO_2 (L) \qquad (6)$$

$$CO_2 (L) \rightarrow CO_2 (gas) \qquad (7)$$

This preceding list of equations, (1) to (7), is given for the purpose of illustration and therefore is not restrictive. But all the possible steps of the reaction considered here may be reduced to one among the seven described types.

For this simple reaction however, the number of possible steps is limited. Furthermore, it is very difficult to justify an order with respect to O_2 varying between one-eight and one-half, if the reaction does not proceed through a step involving oxygen adatoms; an adsorption step including dissociation of oxygen molecules thus seems necessary. In this case all the possible steps leading to CO_2 formation are given by Eqs. (1) to (7).

Moreover, no variation of order results when submitting the catalyst to irradiation. This points to an identical mechanism for both unirradiated and irradiated catalysts.

Among the different reaction steps, one or several are rate-determining and our purpose here is to make explicit these steps.

The true reaction steps (3) to (5) are not rate-determining. Indeed, the principal effect of radiation is to modify the stationary concentration of free carriers and, consequently, the surface concentration of chemisorbed species. Excitation of these chemisorbed species may also take place, either by the free carriers themselves, or by phonons, but the contribution of this phenomenon is very weak. Thermal equilibrium between photogenerated carriers and the lattice is realized after a time of the order of $\sim 10^{-13}$ sec (15), much shorter than the lifetime of these carriers. So the energy content of chemisorbed species having trapped these excess free carriers is probably not different from the normal, thermally chemisorbed, molecules. Neither does one have to take account of the role of phonons generated by radiations. They may interact with

adsorbed molecules and give rise to excitation, but the duration of this excitation is likely very short; the probability of a reaction step involving such an excited molecule is not higher than the triple collision probability for gases.

It thus seems unlikely that the true reaction steps can be activated by radiation, and consequently it is difficult to explain the enhancement of the catalytic activity under irradiation, if reactions of the type (3) to (5) are rate-determining. It must also be noted that the activation energy for reactions (3) to (5) is probably very low. The sole data found in the literature on this subject concern the homogeneous reaction $CO + O \rightarrow CO_2$ (16), which proceeds with an activation energy of 2 kcal. The reaction involving the same species, but one of them at least being in the adsorbed state is probably still less activated. This is an important fact since we have to justify a zero activation energy on irradiated catalyst in a large temperature interval.

It has also been seen that a complementary adsorption of CO_2 is induced by radiation in the temperature interval from 150° to 310°C. Under the same conditions, enhancement of the catalytic activity by irradiation is very important. Therefore, the desorption of CO_2 cannot be rate-determining, in the temperature interval ($200° < T < 360°C$) where the reaction rate can be measured in the absence of irradiation. On the low-temperature side ($20° < T < 80°C$) the desorption rate of CO_2 under irradiation (see Fig. 9) and the reaction rate have about the same value and an important contribution of step (7) is not excluded, but a definitive answer to this question is only possible if the reaction rate without irradiation can be measured at low temperatures.

The conclusion has therefore to be drawn that for temperatures higher than about 100°C, the slow step of the oxidation reaction, is one of the adsorption steps, more clearly one of the chemisorption steps, since the weak adsorption, which does not involve any charge transfer, cannot be influenced by radiation. This as-

sumption is supported by the very important influence of irradiation on the adsorption of the reactants CO and O_2. But, a reaction mechanism involving both CO and O_2 (or O) chemisorbed is not probable, since a migration step of at least one of the chemisorbed species is necessary for the reactions to take place.

This migration step of a chemisorbed molecule is necessarily an activated one and in this case, a zero activation energy cannot be justified under irradiation. It thus seems that the rate-determining step is the adsorption of only one of the reactant gases. The data of adsorption under irradiation will show which of the two gases, either CO or O_2 is concerned. But quantitative correlation between the adsorption rates under irradiation and reaction rates is difficult.
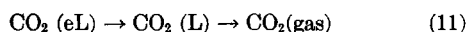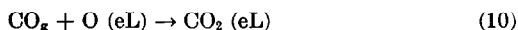
However, it must be noted that the measured rates of adsorption under irradiation correspond to a complex phenomenon where the weak adsorption and the transformation from weak adsorption to chemisorption interfere, only the latter being efficient for the reaction. Furthermore, exact correspondance between adsorption rates, where one molecular species is present in the gas phase, and reaction rates were competition exists between three molecular species, is not possible.

If one takes previous restrictions into account, it is nevertheless interesting to note that, in the particular case of measurements at 25°C, where the value of the reaction rate under irradiation is close to 0.18×10^{-6} moles CO_2 g^{-1} min^{-1}, the adsorption rate of O_2 under the same conditions of pressure and irradiation has a value of $\cong 5 \times 10^{16}$ molecules min^{-1} g^{-1} corresponding to 0.83×10^{-7} moles min^{-1} g^{-1}. Since one molecule of O_2 give rise to the formation of two molecules of CO_2 a very good correlation exists between adsorption and reaction rates.

This fact suggests that the rate-determining step is the oxygen adsorption. Others arguments support this assumption. In a previous paper (9), it has been shown that the alumina used here may be considered, at 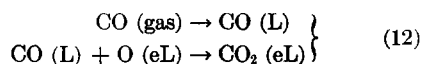least on its surface, as a p-type semi-conductor. Under these conditions, if one admits, like most authors, that the CO molecule has a donor character, the chemisorption of CO must be much easier than that of O_2, the latter being limited by the weak concentrations of free electrons. It should therefore be difficult to justify an activation energy of 18 kcal by proposing, as slow step, the chemisorption of CO.

One is thus led to propose the following reaction mechanism:

$$O_2 \text{ (gas)} \rightarrow 2O \text{ (L)} \tag{8}$$

$$O \text{ (L)} + eL \rightleftharpoons O \text{ (eL)} \tag{9}$$

$$CO_g + O \text{ (eL)} \rightarrow CO_2 \text{ (eL)} \tag{10}$$

$$CO_2 \text{ (eL)} \rightarrow CO_2 \text{ (L)} \rightarrow CO_2 \text{(gas)} \tag{11}$$

where $\rightarrow$ represents a fast step and $\rightleftharpoons$ a slow step, the other symbols having their previous meaning.

In this mechanism step (10) could eventually be replaced by the following sequence, involving a weakly adsorbed form of CO and a surface migration step:

$$\left. \begin{array}{l} CO \text{ (gas)} \rightarrow CO \text{ (L)} \\ CO \text{ (L)} + O \text{ (eL)} \rightarrow CO_2 \text{ (eL)} \end{array} \right\} \tag{12}$$

Under irradiation, the slow step (9) is promoted by the large concentration of produced electrons, and becomes fast. The constancy of the reaction rate, in a large temperature interval, can only be explained if the concentration of free carriers generated by radiation is large in comparison with that existing without irradiation. In this connection, for the lowest intensity used in the present work (55 kV, 1 mA, 2.4×10^{14} eV sec^{-1} g^{-1}) the value of the mean concentration of excess free carriers may be evaluated to 10^9 g^{-1}, assuming for the recombination time the rather low value of 10^{-5} sec. In this calculation, the energy necessary for the formation of a pair of free carriers is estimated to 10 eV (twice the energy gap) (17).

On the other side, the measurements cited in a previous paper (9) indicate that in the temperature range considered here (50 — 350°C) the electrical conductivity of alumina varies between 10^{-10} and 10^{-11} mho cm^{-1}. Assuming for the mobility of free

carriers a value of 1 cm^2 V^{-1} sec^{-1} (18) one calculates that their mean concentration is between 10^8 and 10^9. This evaluation indicates clearly that rather low radiation intensities can modify to an important extent the free carrier concentration in the solid, and in turn, its catalytic properties.

The whole of the experimental results can thus be justified in a qualitative manner by the preceding discussion. Considerable promotion of the catalytic activity by rather low radiation intensity and the possibility of using catalyst irradiation as a new research tool seem to be two major—but only qualitative—conclusions of this work. The quantitative explanation of the observed phenomenon, by aid of the electronic theory of catalysis, remains very difficult, owing probably to a lack of experimental data concerning the electronic structure of the solid.

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