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Carbon Monoxide Oxidation and Adsorbate–Gas Exchange Reactions on MnO_2-Based Catalysts

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The interaction of gaseous carbon monoxide, carbon dioxide, and oxygen with MnO_2 catalysts was studied by means of chemisorption and isotope exchange reactions. The results show that oxidation of carbon monoxide by lattice oxygen of MnO_2 is a rapid process producing gaseous and to some extent also adsorbed carbon dioxide, the following reoxidation being a very difficult reaction step. This behavior is markedly different from that of NiO and MnO. When platinum is introduced by hydrosol precipitation onto the surface of MnO_2, the reactivity of the catalyst towards carbon monoxide and oxygen considerably increases and strongly adsorbed CO is detected, in contrast to pure MnO_2.

INTRODUCTION

MnO_2-based catalysts are the most active ones for the oxidation of carbon monoxide (*1*, *2*). The mechanism of this reaction goes through intermediates of more or less uncertain composition. With another active catalyst, namely nickel oxide, an attempt has recently been made to identify at least some of the adsorbed species in the reaction considered by means of exchange reactions with the use of radiocarbon (*3*). This method is based on the fact that CO(ads) as well as CO_2(ads) are able to exchange only with molecules of their own kind. The present work makes use of this analysis by exchange, combined with chemisorption and electric conductivity measurements, in the investigation of the individual reaction steps in CO oxidation on MnO_2 and some MnO_2-based catalysts. The behavior of CO, O_2, and CO_2 at low pressures (10^{-3}–10^{-1} torr) on the surfaces of MnO_2, pure and doped with Pt, Ag, and CuO, is described.

EXPERIMENTAL

Materials. The preparation of the gases used, namely, oxygen, carbon monoxide, and carbon dioxide, is described elsewhere (*4*), as well as the methods of obtaining the catalysts based on MnO_2 (*5*). Pure manganese dioxide was prepared by the Frazer method (*5*, *6*). The surface area of the product was about 250 m^2/g (Kr, BET). Impregnation of the MnO_2 powders with surface admixtures was effected by precipitation from the corresponding hydrosol. It should be noted that the sols used were free from stabilizing electrolytes. The advantages of this method of impregnation are a finely dispersed clean deposit, no adsorption of electrolytes, and no reduction or dissolution of surface layers by reagents used in the conventional precipitation procedures (*5*). Electron micrographs of the doped catalysts indeed show the particles of admixtures to be finely dispersed on the surface of MnO_2 granules. The admixtures used were CuO (2 wt %), Ag (3 wt %), and Pt (6 wt %).

Manganous oxide MnO used for comparative measurements was prepared by decomposing the corresponding carbonate *in vacuo* at 380°C.

Apparatus. All measurements were carried out in a closed-volume apparatus (1800 ml). Pressure changes were measured by a Pirani gauge forming a branch of a DC Wheatstone bridge; desorbed amounts were determined by means of a gas collection pump. Electric conductivity of the powdered samples was measured by a high-frequency loss angle meter RFT 193 Erfurt (Germany), the catalyst being placed between two parallel gold electrodes 2 mm apart. The exchange reaction with radiocarbon was followed by a GM counter set close to a thin mica window (1 mg/cm^2) cemented to the glass apparatus wall by Araldite (Fig. 1). The calibration graphs of activity vs. pressure were linear, as may be seen from the graph in Fig. 2.

Procedure. Labeled carbon monoxide was first admitted to the catalyst powder at an initial pressure of 6.6×10^{-2} torr and temperature 20°C. Carbon dioxide formed by reaction of CO with the oxide surface was immediately frozen out in cold traps at —195°C. The pressure of the noncondensable carbon monoxide thus decreased in the course of reaction. The process was interrupted when the rate of $C^{14}O$ uptake dropped to 0.1 mole/hr, which was slow enough to ensure convenient conditions for carrying out the subsequent exchange reactions. In most cases two portions of gas had to be admitted, the first of them having been consumed to zero pressure. Hereafter desorbable carbon monoxide was pumped off by the gas collection pump, its amount measured in a separate volume, and removed from the system. The $C^{14}O_2$ condensed in the freezing traps was then evaporated by changing the temperature of the traps to —78°C, its amount determined

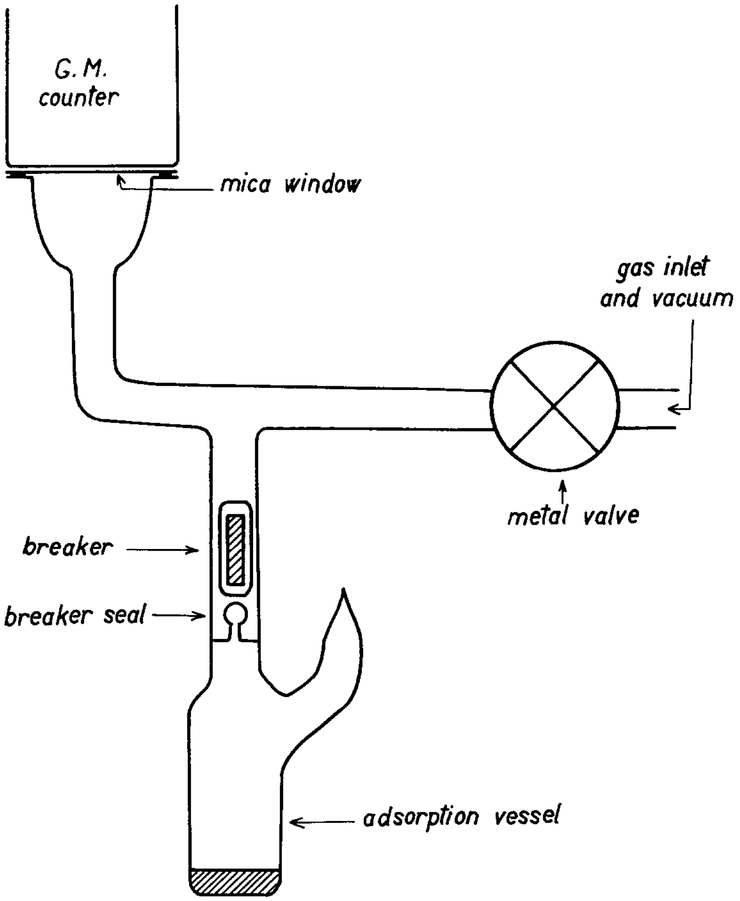


FIG. 1. Apparatus for measurement of exchange reactions.

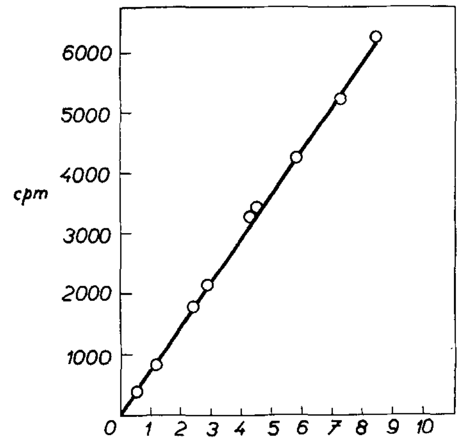


FIG. 2. The measured count rate (cpm) of $C^{14}O$ as a linear function of pressure.

from pressure and again pumped out of the system. Afterwards, the exchange reaction was commenced by admitting $C^{12}O$ to the sample at about the same initial pressure and temperature as $C^{14}O$ before, with the cold traps at liquid nitrogen temperature. The rise of radioactivity in the gas phase was then followed. The proper measure of the degree of exchange is the specific radioactivity (gas radioactivity divided by pressure), which allows for eventual pressure variations. When the specific radioactivity reached a steady value, carbon monoxide was pumped off and the amount of carbon dioxide formed during the exchange reaction was measured with cold traps at —78°C. After removal of this CO_2 of mixed isotopic composition, $C^{12}O_2$ was admitted to the catalyst at 20°C and pressure of $3–4 \times 10^{-2}$ torr and allowed to exchange with the adsorbate. The course of the process was followed in the same way as in the case of CO. Afterwards, the apparatus was evacuated and oxygen admitted to the powder at initial pressure of 5.5×10^{-2} torr. The gas was allowed to react first at 20°C for 75 min; the temperature was then raised to 100°C for additional 95 min, the cold traps being all the time kept at —195°C.

For measurements of electric conductivity carbon monoxide was admitted to pure MnO_2 at initial pressure of 1×10^{-1} torr and the change of resistance was followed with time. The values were taken at the frequency of 1 Mc/sec. Analogous procedure was carried out with MnO_2 in oxygen at pressures 6.5×10^{-2} torr. In this case the resistance of pure as well as CO surface-treated samples was determined. The type of semiconductivity of MnO_2 was estimated by establishing a temperature difference between two inert electrodes immersed in the oxide powder and detecting the polarity of the ensuing Seebeck voltage.

RESULTS AND DISCUSSION

Interaction of MnO_2 with CO

Pure MnO_2 shows a remarkable reactivity towards carbon monoxide. At the low pressures used, oxidation of carbon monoxide may be observed at temperatures as low as —78°C and proceeds readily at 0°C and 20°C. The time course of CO uptake at 20°C is shown in Fig. 3 together with the results for Pt-MnO_2 catalysts. The reaction product CO_2 tends to leave the surface even if it is not removed from the gaseous phase by condensation; thus only a small coverage by residual adsorbate is achieved during the reaction of MnO_2 with CO.

In order to estimate the qualitative and quantitative composition of the residual adsorbate we employed exchange reaction with gaseous CO and CO_2 as described above and in ref. (*3*). The results obtained are summarized in Table 1. One marked feature of the present system is that labeled adsorbate does not exchange at all with gaseous carbon monoxide at 20°C. On the other hand, there is an extensive exchange of the adsorbate with gaseous carbon dioxide at the same temperature upon the appearance of $C^{14}O_2$ in the gas phase (Fig. 4). The results of these observations are independent of the sequence of exchanging gases (CO–CO_2 and CO_2–CO) and they therefore indicate that the adsorbate produced on the MnO_2 surface during interaction with carbon monoxide consists entirely of CO_2(ads). The gas desorbed by pumping at 20°C contains hardly detectable amounts of carbon monoxide (Table 1, col. 3). At —78°C the situation is somewhat different;

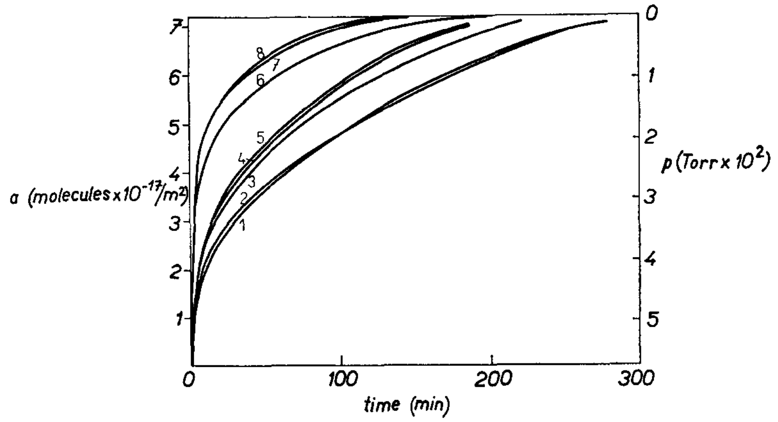


FIG. 3. The time course of CO uptake by different samples of MnO_2 (curves 1–5) and Pt-MnO_2 (curves 6–8); *a*, amount of CO consumed; *p*, pressure of CO in apparatus.

TABLE 1

DATA ON INTERACTION OF CO AND O_2 WITH MnO_2 CATALYSTS[a]

Sample	CO uptake	CO desorbed	CO_2 frozen out	CO_2 (ads) according to exchange	CO (ads) according to exchange	Non-exchanging adsorbate	O_2 adsorbed	
							20°C	100°C
MnO_2 I	13.1	0.04	11.7	*b*	0.0	*b*	0.6	1.4
MnO_2 II	12.1	0.02	10.8	0.9	*b*	0.4	0.4	1.0
MnO_2 III	12.7	0.10	11.3	0.8	*b*	0.5	0.4	1.2
MnO_2 IV	12.9	0.02	11.4	*b*	*b*	*b*	*b*	*b*
MnO_2 V	12.3	0.012	11.1	0.7	*b*	0.4	0.1	*b*
Pt-MnO_2 I	11.8	0.18	9.7	1.0	*b*	*b*	0.8	1.6
Pt-MnO_2 II	12.6	0.06	10.2	1.0	*b*	*b*	0.7	1.4
Pt-MnO_2 III	13.3	0.04	11.0	0.6	*d*	*b*	0.9	1.3
Ag-MnO_2 I	13.4	0.00	11.8	*b*	*b*	*b*	0.8	1.6
Ag-MnO_2 II	6.6[c]	0.08	5.3	0.4	0.0	0.9	0.6	1.3
CuO-MnO_2	6.6[c]	0.002	5.8	0.4	0.006	0.3	*b*	*b*

[a] All figures are given in molecules $\times 10^{-17}/m^2$.

[b] Not determined.

[c] One admission only.

[d] Exchange of adsorbate with CO(g); see Fig. 7.

there is some CO(ads) present, which suggests that the oxidation reaction is a consecutive process having molecular CO adsorption as its first step, followed by oxidation of the adsorbed species with surface oxygen of MnO_2 and escape of the major part of the product CO_2 to the gas phase.

The exchange kinetics of carbon dioxide (Fig. 4) show a slow approach of the specific activity towards the stationary value which will be treated as exchange equilibrium for the purpose of quantitative estimates of adsorbate composition. The curve strongly deviates from the exponential law

$$X/X_\infty = 1 - \exp(-\alpha t)$$

which should be obeyed if the adsorbate were energetically homogeneous (7). (X is the specific radioactivity of the gas at time t.) Furthermore, material balance reveals that at 20°C a part of the adsorbate exchanges with neither of the carbon oxides (Table 1, col. 7); from this part carbon dioxide can be recovered by desorption at 100°C, having specific radioactivity higher

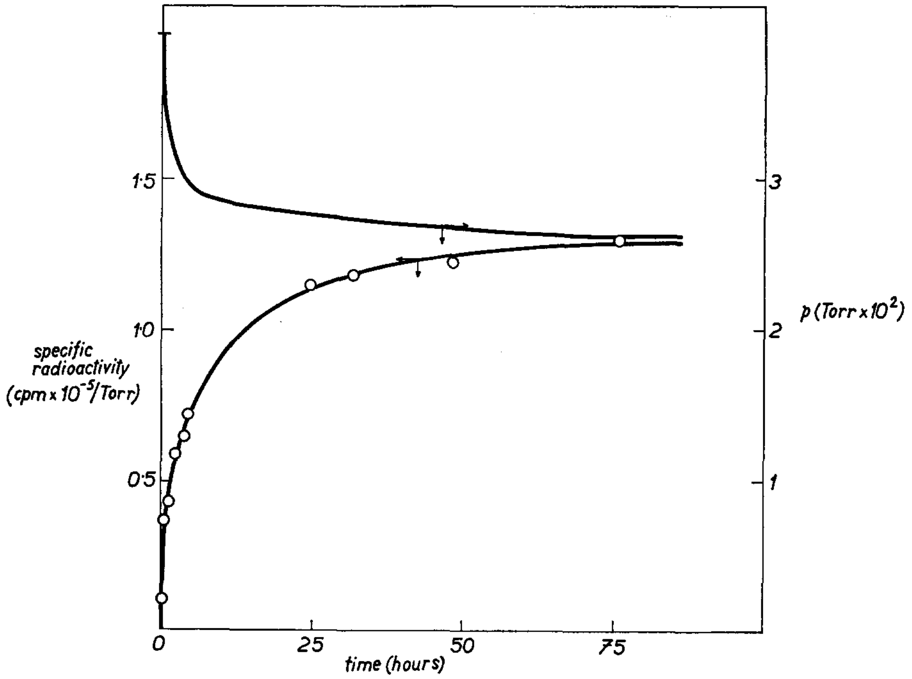


FIG. 4. Typical time course of exchange of labeled adsorbate with $CO_2(g)$ on MnO_2 (0.020 g of surface area 5 m^2). $X_0 = 7.05 \times 10^5$ cpm/torr; $X_\infty = 1.36 \times 10^5$ cpm/torr; $g + b = 1.84 \times 10^{18}$ molecules; $m = 4.4 \times 10^{17}$ molecules. The meaning of the symbols used is explained in the text. Upper curve: pressure of CO_2 during exchange (right-hand scale); lower curve: specific radioactivity of CO_2 (g) during exchange (left-hand scale).

than the "equilibrium" one after the exchange with $C^{12}O_2$. This part of the CO_2 adsorbate may be regarded as an extreme case of heterogeneous bonding. In the surface of MnO_2 is thus produced a wide spectrum of CO_2(ads) species covering a range between easily desorbing molecules and those which do not even exchange at 20°C with gaseous carbon dioxide.

Quantitative composition of the adsorbate may be derived from equilibrium values of specific radioactivity after the exchange as follows: The exchange reaction has reached equilibrium when the isotope is uniformly distributed between the gaseous phase and that portion of adsorbate which takes part in the exchange. The specific radioactivity (most conveniently expressed here is cpm/torr) of all exchanging partners then becomes constant even when pressure may still decrease due to adsorption of exchanging gas. For the procedure presently employed, i.e., adsorbate is labeled and the gas unlabeled at the beginning of exchange, the condition for uniform distribution of isotope is [cf. also ref. (*3*)]

$$X_\infty/X_0 = m/(g + b + m),$$

where m is the number of adsorbed molecules, having the specific radioactivity X_0 before exchange, which are able to exchange with a given unlabeled gas. The quantities g and b are the numbers of molecules of this originally unlabeled compound in the gas and adsorbate, respectively; $g + b$ represents its total amount admitted. X_∞ is the specific radioactivity measured after isotopic equilibrium had been reached with this newly admitted gas. From measured X_0, X_∞, and $g + b$ one can calculate m.

In our case the adsorbate was formed by surface reaction of $C^{14}O$ of specific radioactivity X_0 with MnO_2 and was subjected to exchange with unlabeled $CO_2(g)$. Therefore *m* is the number of exchanging adsorbed CO_2 molecules, which is given in the fifth column of Table 1.

Chemisorption of CO_2

Apart from the surface oxidation of CO, adsorbed carbon dioxide can be produced simply by CO_2 adsorption. This process was followed in the 10^{-2} torr pressure range at temperatures from −78° to +100°C. The adsorption is slow and the adsorbate is to a large extent irreversibly bound. CO_2 adsorbed at 0°C cannot be recovered at 20°C (Fig. 5). In accordance with the observed small retention of the CO_2 produced by oxidation, the amounts adsorbed from CO_2 gas are also small, namely, of the same order of magnitude as the coverages resulting from the reaction with CO.

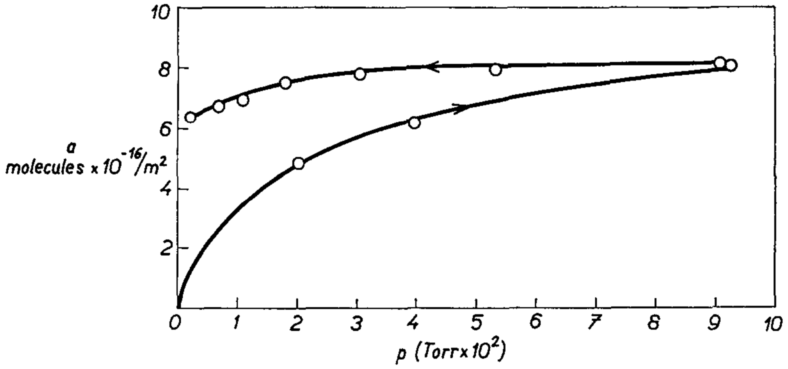


FIG. 5. Adsorption isotherms of CO_2 on MnO_2. Lower branch, 0°C, adsorbed amounts (*a*) measured with increasing pressure (*p*); upper branch, 20°C, adsorbed amounts measured with decreasing pressure.

The low affinity of the greater part of MnO_2 surface towards CO_2 is understandable in view of the chemistry of Mn(IV). No carbonates of quadrivalent manganese are known, which fact is obviously due to the low basicity of MnO_2. On the other hand, basic oxides such as NiO (*3*) and CoO (*8*) which form carbonates, also adsorb very strongly large quantities of CO_2. In this respect, the small but tightly bound CO_2 adsorbate on MnO_2 presents a problem as to the exact nature of the adsorption sites involved. These are probably not connected with lower valencies of manganese because the amount of CO_2 bound to the original and reduced surfaces is the same. The possibility that, e.g., $MnCO_3$ is formed by some reaction of CO_2 with MnO_2 seems unlikely since no evolution of oxygen was observed during CO_2 adsorption.

Oxygen Chemisorption

The MnO_2, even with its surface reduced, is relatively inert towards oxygen. Pure MnO_2 surface does not show any tendency to adsorb oxygen up to 100°C in the 10^{-2} torr pressure range. Manganese dioxide whose surface was partially reduced by reaction with CO chemisorbs a small amount of oxygen at 20°C. This extent is increased by raising the temperature to 100°C but again the effect is slight. The amount of oxygen adsorbed is always much less than that removed from the surface by CO so that the surface is only partially reoxidized (Table 1). This observation is in good qualitative agreement with that recently reported by Brooks (*9*), namely that oxygen-depleted surfaces of MnO_2 do not completely build up the oxygen content even at 410°C. Under the present experimental conditions oxygen consumption proceeds by an initial rapid adsorption at 20°C followed by a very slow decrease of pressure. At 100°C the latter process is accelerated, which points to an activated character of this adsorption.

Evidence for Electron Transfer by Electric Conductivity Measurements

The measurements of electric conductivity changes are made somewhat difficult by the fact that MnO_2 itself is a fairly conducting powder so that slight changes in current carrier concentration due to charge transfer in the surface do not affect measurably its resistance. Thus no difference in this property was observed after oxygen adsorption on prereduced manganese dioxide. On the other hand, the reaction of the surface with carbon monoxide is accompanied by a slow decrease of resistance (Fig. 6). As our powder was shown to be an *n*-type semiconductor by the sign of the Seebeck effect, the observed rise in conductivity indicates that electrons are released into the lattice in accordance with the overall scheme shown below. The electrons on the right reduce the Mn^{4+} ions to some lower valency state of manganese, e.g., Mn^{3+}, well known from the stable oxide Mn_2O_3 (*10*). Further arguments in favor of Mn^{3+} in oxygen-depleted MnO_2 have been put forward in ref. (*9*). The electrical conductivity could then be effected by electron transfer between Mn^{3+} and Mn^{4+} in an electric field.

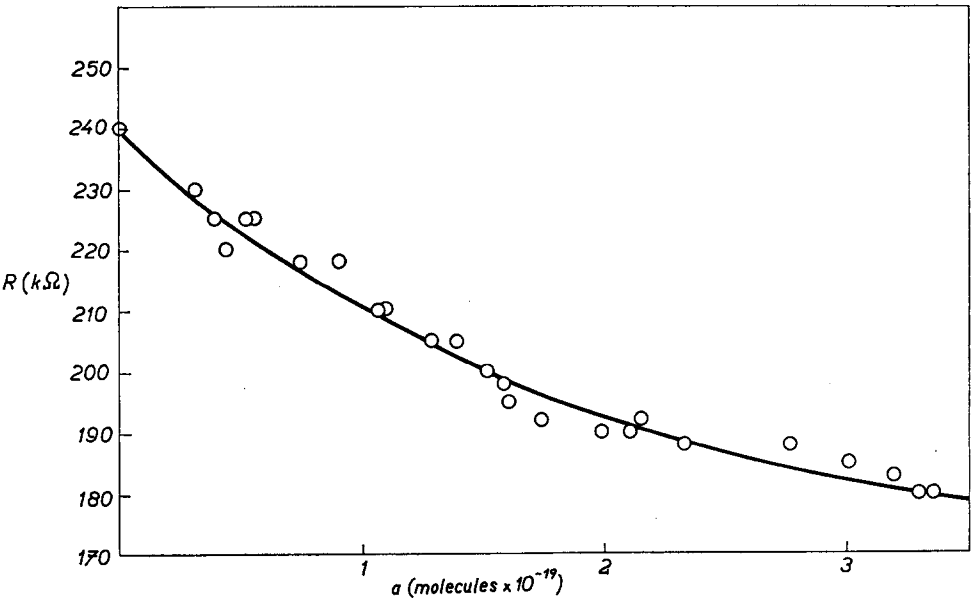
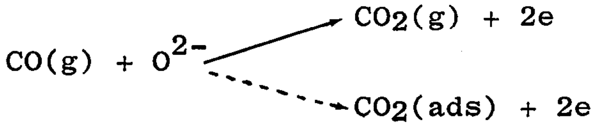


FIG. 6. The dependence of electric resistance (R) on the CO uptake (a) by MnO_2 catalyst (0.327 g).

Remarks Concerning the Reaction Mechanism on Various Oxides

The main features of carbon monoxide oxidation by oxygen on the surface of MnO_2 under the conditions employed can be summarized as follows:

(1) easy oxidation of CO by the surface oxygen of MnO_2;
(2) rapid release of most of the CO_2 formed to the gas phase;
(3) difficult reoxidation by gaseous oxygen of the surface reduced by process (1) and exposed by process (2).



This behavior of manganese dioxide is basically different from that of another catalytically active oxide NiO where oxygen chemisorption and subsequent carbon monoxide oxidation are relatively rapid processes whereas the product CO_2 remains strongly bound to the surface, desorption of CO_2 thus being the rate-limiting step (*3*). There are some additional differences between the two catalysts, e.g., the presence of CO(ads) on the surface of nickel oxide which, however, strongly depends on the amount of preadsorbed oxygen ions. The situation in the surfaces of the two catalysts is best represented by Fig. 7.

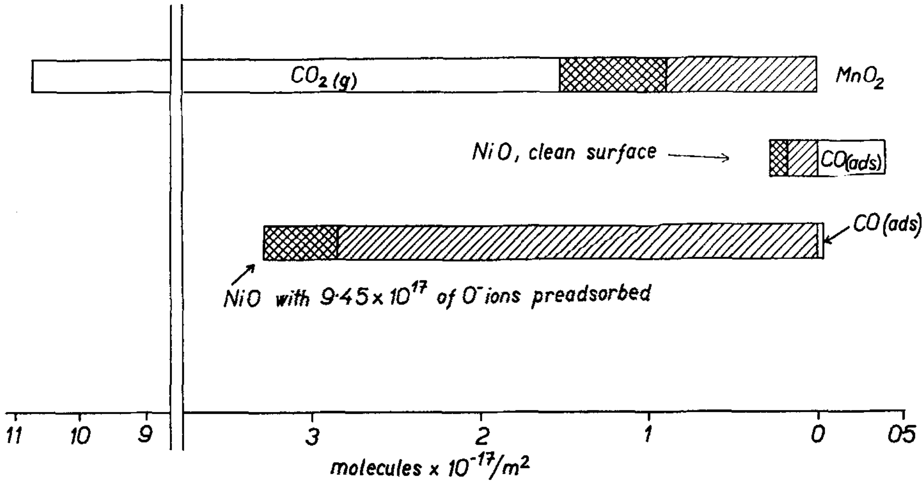


FIG. 7. Catalyst surfaces: CO_2(g), desorbing CO_2; CO(ads), adsorbed CO; diagonal lines, adsorbed CO_2 exchanging with CO_2(g); cross-hatching, nonexchanging adsorbate.

Some experiments were also made with manganous oxide, MnO, which is related to MnO_2 chemically but also resembles NiO in many respects (structure, valency). Its reactivity towards oxygen and carbon dioxide surpasses that of NiO. A clean surface of MnO (40 m^2/g, Kr, BET) took up more than three monolayers of oxygen atoms (pressure range 10^{-2} torr, 7×10^{18} molecules/m^2 at $-78°C$, 5×10^{18} molecules/m^2 at 20°C, and 7×10^{18} molecules/m^2 at 100°C) and in air proved pyrophoric. Adsorption of CO_2 was also extensive (pressure range 10^{-2} torr, 5.6×10^{18} molecules/m^2 at 20°C) and its reversibility decreased with time (11% of adsorbate was recovered by 30 min pumping after 7 min of adsorption, 2% after 1 hr, and 1% after 2 hr).

The foregoing results show that the individual steps of the same catalytic reaction proceed with rates so much different from one catalyst to another that the rate-limiting step varies with the different oxides. The fact itself is not surprising but is emphasized here because of the lack of attention it receives in the theory of catalysis.

The respective rates of interaction with O_2 and CO_2 of the individual oxides may be tentatively related to the valency state of their cations. So the low oxides (MnO, NiO) tend to be readily oxidized and at the same time their basic character is responsible for extensive adsorption of CO_2. These two tendencies decline with increasing oxidation state of the cation in oxides; thus MnO_2 is easily reduced, difficult to oxidize, and adsorbs but little CO_2.

Mixed Catalysts

As a commercial catalyst for CO oxidation MnO_2 is always used with promotors such as Co_2O_3, CuO, Ag_2O, etc. Some of these are incorporated in the bulk, others in the surface of MnO_2 (*11*). An interesting problem emerges concerning the possible specific influence of these two types of promotion. We studied the effect of surface dopes on the behavior of MnO_2 catalysts. Only a single additive was used in all cases. CuO was chosen as representative of the usual oxide admixtures; this was compared with the effect of surface metal deposits of Ag and Pt. Of these three additives a markedly different behavior is displayed only by platinum. Its presence leads to a much more rapid uptake of carbon monoxide (Fig. 3) following a different kinetic law (*5*). The resulting adsorbate exchanges with gaseous CO, as shown in Fig. 8, which brings about evidence that some carbon monoxide remains adsorbed at 20°C without being oxidized, in distinction from pure MnO_2. The slow progress of exchange indicates a strong bonding of the CO molecule to the surface. Since the presence of the CO adsorbate was induced by addition of platinum, it is very likely that CO adsorption takes place directly on the surface of the metal. Because of the low rate of exchange with CO the reaction was far from equilibrium when interrupted and therefore the amount of CO(ads) could not be determined.

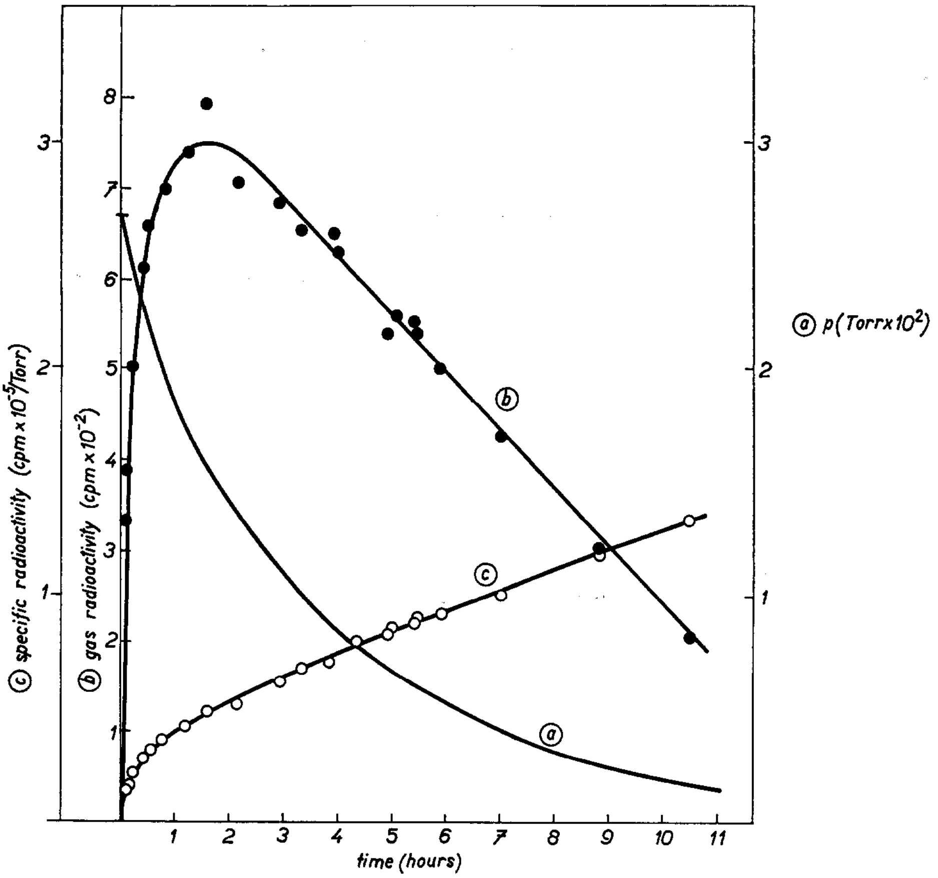


FIG. 8. The exchange of labeled adsorbate with CO(g) on Pt-MnO_2 catalyst (0.020 g of surface area 5 m^2); *p*, pressure of CO(g) during exchange.

A substantial part of the adsorbate exchanges with gaseous carbon dioxide (Fig. 9). The course of exchange is similar to that on pure MnO_2, which suggests that this adsorbate originates by the reaction of CO with the remaining MnO_2 surface.

The other mixed catalysts investigated do not exhibit qualitative difference from the undoped oxide with regard to the adsorbate composition. With CuO–MnO_2 there

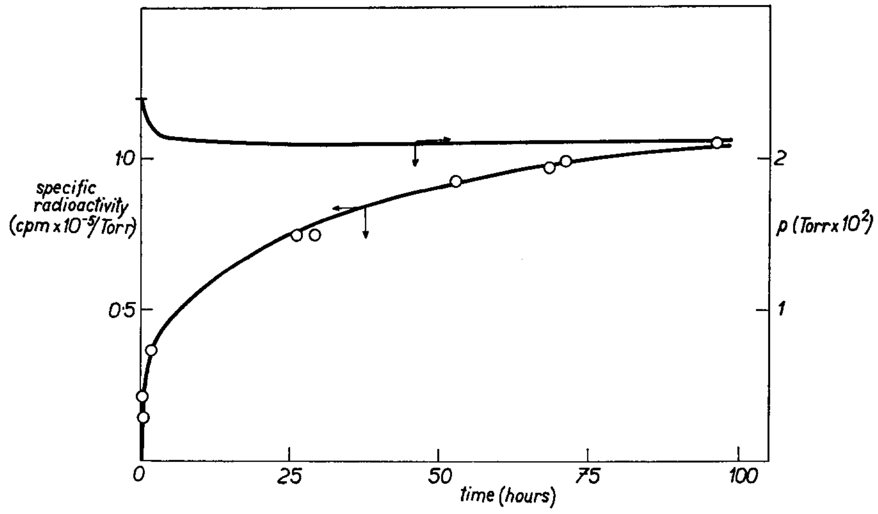


FIG. 9. The exchange of labeled adsorbate with $CO_2(g)$ on Pt-MnO_2 catalyst (0.020 g of surface area 5 m^2). $X_0 = 7.05 \times 10^5$ cpm/torr; $X_\infty = 1.34 \times 10^5$ cpm/torr; $g + b = 1.37 \times 10^{18}$ molecules; $m = 3.2 \times 10^{17}$ molecules. The meaning of the symbols used is explained in the text. Upper curve: pressure of CO_2 during exchange (right-hand scale); lower curve: specific radioactivity of $CO_2(g)$ during exchange (left-hand scale).

is only a very small part of adsorbate exchanging with carbon monoxide (6×10^{14} molecules/m^2, Table 1); with Ag-MnO_2 no detectable CO exchange takes place. Also the rate of CO uptake and its kinetics (*5*) do not appreciably differ. There are, however, slight differences in reacted amounts, which may be seen from Table 1. Because of the relatively poor reproducibility of these results (*5*) it is not certain whether there are any significant promotion or retardation effects in the case of copper oxide and silver.

REFERENCES

1. KATZ, M., *Advan. Catalysis* **5**, 177 (1953).
2. DIXON, J. K., AND LONGFIELD, J. E., *in* "Catalysis" (P. H. Emmett, ed.), Vol. VII, p. 281. Reinhold, New York, 1960.
3. KLIER, K., AND JIRATOVA, M., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, p. 763 (1965).
4. KLIER, K., *Kinetika i Kataliz* **3**, 65 (1962).
5. NAJBAR, M., KUCHYNKA, K., UND KLIER, K., *Coll. Czech. Chem. Commun.* **31**, 959 (1966).
6. WHITESELL, W. A., AND FRAZER, J. C. W., *J. Am. Chem. Soc.* **45**, 2841 (1923).
7. EISCHENS, R. P., *J. Am. Chem. Soc.* **74**, 6167 (1952).
8. RUDHAM, R., AND STONE, F. S., *in* "Chemisorption" (W. E. Garner, ed.), p. 205. Butterworths, London, 1957.
9. BROOKS, C. S., *J. Catalysis* **4**, 535 (1965).
10. MOORE, T. E., ELLIS, M., AND SELWOOD, P. W., *J. Am. Chem. Soc.* **72**, 856 (1950).
11. LAMB, A. C., BRAY, W. C., AND FRAZER, J. C. W., *Ind. Eng. Chem.* **12**, 213 (1920).