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The Catalytic Oxidation of Carbon Monoxide on Tin(IV) Oxide

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The oxidation of carbon monoxide has been investigated on catalysts obtained by thermal activation of granular hydrous tin(IV) oxide gel in the temperature range 200–500°C. These are active for this reaction at moderately low temperatures (<150°C). Thermogravimetry and nitrogen adsorption have been used to investigate the water content and specific surface areas of the activated catalysts, and these parameters have been related to the initial catalytic activities. The partial deactivation during carbon monoxide oxidation at low temperatures, which is apparently accompanied by partial reduction of the catalyst surface, has been studied as a function of both the activation and reaction temperatures. The kinetics of the steady state reaction have been investigated at 180–210°C on the 450°C-activated catalyst, and the postulated mechanism involves adsorption of carbon monoxide, desorption of carbon dioxide and oxygen regeneration of the catalyst. The kinetics can be represented by the Langmuir-type rate equation, similar to that derived for the same reaction on both V_2O_5 and Fe_2O_3, and this permits evaluation of the experimental activation energies for the adsorption and desorption steps.

INTRODUCTION

The catalytic oxidation of CO has been studied on numerous simple and mixed oxide catalysts over the years, and this subject has been extensively reviewed (*1–4*). Although the earlier investigations into the catalysis of this reaction were conducted mainly to obtain theoretical insight into the mechanism of oxidation on oxide catalysts, there has recently been a resurgence of interest in this subject in connection with its possible application to the purification of automobile exhaust gases.

With the exception of a brief report by Yoneda and Makishima (*5*), there are no data available for the catalysis of CO oxidation on SnO_2. This is somewhat surprising, since our preliminary investigations showed SnO_2 to be active for this reaction at moderately low temperatures (<150°C) (*6*). For this reason a more detailed study of this reaction on SnO_2 was undertaken.

METHODS

Catalyst Preparation

The catalyst was precipitated as hydrous SnO_2 by the dropwise addition of AnalaR concentrated aqueous ammonia solution to a cold, vigorously stirred solution of $\sim$0.6 *M* redistilled $SnCl_4$ in water, to a final pH of 4. The precipitate was repeatedly centrifuged and redispersed in distilled water until peptization of the precipitate was imminent, then again centrifuged and allowed to dry in air at ambient temperature. The large granules were broken down by immersion in water, column washed over several days with 1 *M* HNO_3, then column washed with water to an effluent pH of 4–5 to give an essentially ion-free, granular gel. The granules were then dried in air, firstly at ambient temperature, then at 200°C, and stored in a desiccator over activated silica gel.

Catalytic Studies and Gas Analyses

The catalytic reactor was of the up-flow type, consisting of an 11-mm diameter Pyrex tube containing a sintered-glass support and attached to a preheating coil wound from an 80-cm length of 2.5-mm i.d. Pyrex tubing. Ground glass joints were used for feed gas, sampling and manometer attachments. The reactor was heated by means of a 25-mm diameter quartz tube specially wound with nichrome wire and supplied by a Eurotherm temperature controller to produce an even and constant (±0.5°C) temperature over the catalyst bed, the temperature of which was measured using N.P.L.-calibrated mercury-in-glass thermometers.

Cylinders of C.P. grade Ar, CO, CO_2, N_2 and air were used as supplied, and the feed-gas flow rates were measured using Rotameter flow meters. All feed gases were dried by passing them successively through columns of silica gel and molecular sieve type 5A pellets (preactivated in a dry air stream at 170 and 300°C, respectively) and (except for studies using CO_2 in the feed) KOH pellets, using an all-glass feed line. The water contents of the gases dried by this method were <5 ppm.

Unless otherwise stated, 36–72 B.S.S. mesh catalyst granules were used, and thermal activation was carried out in the reactor in a stream of dry air.

The product gases were analyzed for CO_2 (up to 5% concentration) by on-line chromatography using a Perkin–Elmer F11 gas chromatograph with hot-wire detectors. Helium was used as the carrier gas, and the CO_2 was chromatographed on a silica gel column at 150°C. The chromatograph was calibrated using standardized CO_2–Ar mixtures. The products were then collected, via the chromatograph sampling valve, over 5% H_2SO_4 (which provided an accurate measure of the product flow rates) and then transferred to an Orsat gas analysis apparatus for volumetric O_2, CO and (for concentrations above 5%) CO_2 analysis.

A preliminary experiment showed that the empty reactor gave no oxidation of CO for temperatures up to at least 500°C.

Physical Characterization

Specific surface areas were obtained from nitrogen adsorption data in the B.E.T. region using the method and apparatus similar to those described by Haul and Dümbgen (7).

Thermogravimetric analysis was obtained under equilibrium conditions by heating the same sample of SnO_2 gel in a dry air stream to constant weight for a series of increasing temperature steps.

Transmission ir spectra were obtained from discs of 1% catalyst in KBr using a Grubb Parsons Spectromaster.

X-ray powder data were obtained with a Philips Debye–Scherrer, 11.64-cm camera using filtered Cu$K\alpha$ radiation.

Chemical Analysis

A measure of the degree of reduction of partially reduced SnO_2 catalysts was obtained by dissolving 1–2 g samples in 20 ml of gently refluxing HBr solution (AnalaR, S.G. 1.48). The HBr was rendered oxygen free by refluxing it for some time in a stream of oxygen-free nitrogen before addition of the catalyst, and the dissolution was carried out under nitrogen. After dissolution the solution was cooled under nitrogen in an ice bath, diluted to 50 ml with cold, air-free water and titrated with iodide–iodate solution using starch indicator.

RESULTS

Nonequilibrium Catalytic Studies

Calcination of hydrous SnO_2 gel in air at temperatures between 200 and 500°C, which results in a darkening in color of the material from pale yellow to orange, yields products which show high initial activity for CO oxidation at low temperatures, as shown in Fig. 1. To obtain these data the catalyst samples were activated in the reactor at various temperatures in a stream of dry air. After introduction of the CO the temperature was lowered, and the CO oxidation was monitored for de-

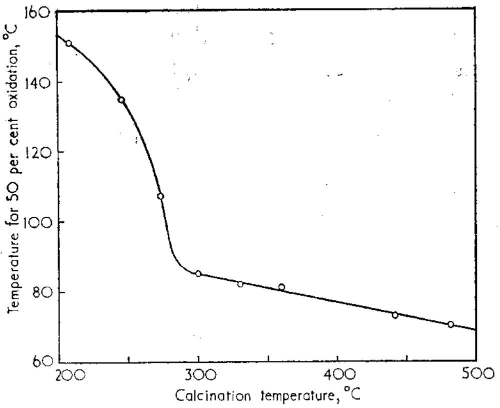

FIG. 1. Effect of calcination temperature on initial CO-oxidation activity of SnO_2 gel. 6–7% CO in air feed through 6 ml (12.6 g) SnO_2 bed at flow rate of 96 cm^3 min^{-1}.

creasing temperature steps. All determinations were made within one hour after activation, and the 50% CO oxidation temperatures were obtained, for each activation temperature, from plots of % oxidation vs reaction temperature.

Figure 2 shows the effect of calcination temperature on two parameters which would be expected to influence the CO oxidation activity of calcined SnO_2 gel, viz, the static T.G. (water content) curve, and the B.E.T. specific surface area. During calcination of the SnO_2 gel the only crystalline phase detected by X-ray diffraction was that of cassiterite (mineral SnO_2), the degree of crystallinity increasing with increasing calcination temperature. These observations are in agreement with those of Goodman and Gregg (*8*) and Vincent and Weston (*9*), and contrast with the electron-diffraction results of Giesekke *et al.* (*10*), which indicated the existence of a series of crystalline phases during calcination of hydrous SnO_2 gel.

A marked increase in the initial catalytic activity of calcined SnO_2 gel occurs on increasing the activation temperature from 200 to 300°C (Fig. 1) and Fig. 2 shows that, between these temperature limits, a marked reduction (65%) in the water content of the catalyst occurs, accompanied by a relatively much smaller decrease (25%) in its specific surface area. For activation temperatures above 300°C, however, the reduction in surface area due to sintering becomes very marked, and is accompanied by a leveling off in the CO oxidation activity of the freshly activated catalyst. This indicates a compensating effect of the decreases in both water content and surface area which occur on increasing the calcination temperature between 300 and 500°C.

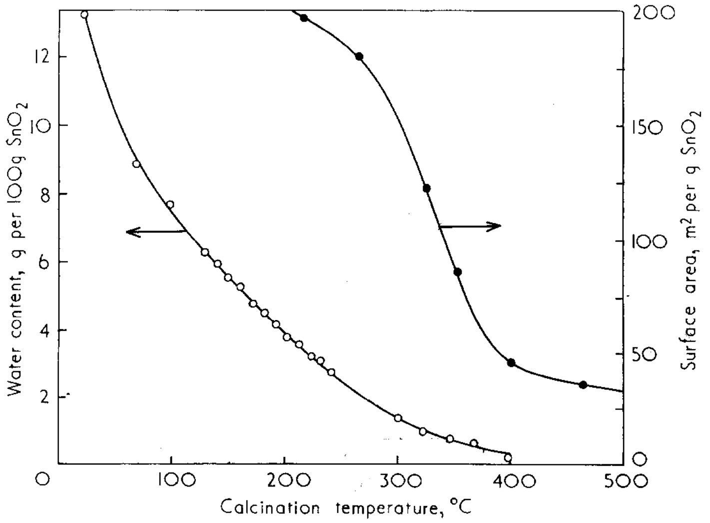

FIG. 2. Effect of calcination temperature on the equilibrium water content and the specific surface area of SnO_2 gel.

Deactivation Studies

The above studies have shown that, up to at least 500°C, a high calcination temperature favors high initial CO oxidation activity of freshly activated SnO_2 gel. However, experiments over longer periods showed that, under certain conditions, calcined SnO_2 gel undergoes partial deactivation during CO oxidation catalysis, accompanied by a darkening in color of the catalyst. Under conditions where only slight deactivation occurs, the catalyst assumes a pale brown color, whereas conditions favoring more extensive deactivation produce increased darkening of the catalyst to, in the most extreme cases, a black color. The color of the catalyst partially deactivated to steady state in CO–air mixtures becomes increasingly darker with (a) an increase in the initial activation temperature of the gel (between 200 and 500°C) and (b) a decrease in the temperature at which the reaction is carried out.

These effects are illustrated in the deactivation curves of Fig. 3. For the gel calcined at 210°C deactivation only becomes significant for reaction temperatures below about 200°C, and even at 150°C the steady state catalyst had darkened only slightly. The gel calcined at 450°C, however, was found to deactivate significantly at reaction temperatures below about 300°C, and at 200°C this effect was very marked, resulting in a brown-black steady state catalyst.

In all instances where deactivation occurred, the steady state catalysts returned to their higher initial activities after thermal reactivation in air.

Steady State and Kinetics Studies

Although the above studies have shown that calcined SnO_2 gel undergoes partial deactivation during low-temperature catalysis of CO oxidation, it was found that, for reaction temperatures at least as low as 150°C, the steady state catalysts showed excellent stability, and could be used over long periods without showing significant variations in catalytic activity.

Most of the subsequent catalytic studies described here were conducted on SnO_2 gel activated at 450°C (specific surface area (S) = 36 m^2g^{-1}) and preequilibrated to steady state. This activation temperature was chosen to give an essentially anhydrous catalyst (see Fig. 2), although some interesting comparisons between the catalytic properties of this material and the partially hydrated, 210°C-calcined gel (S = 190

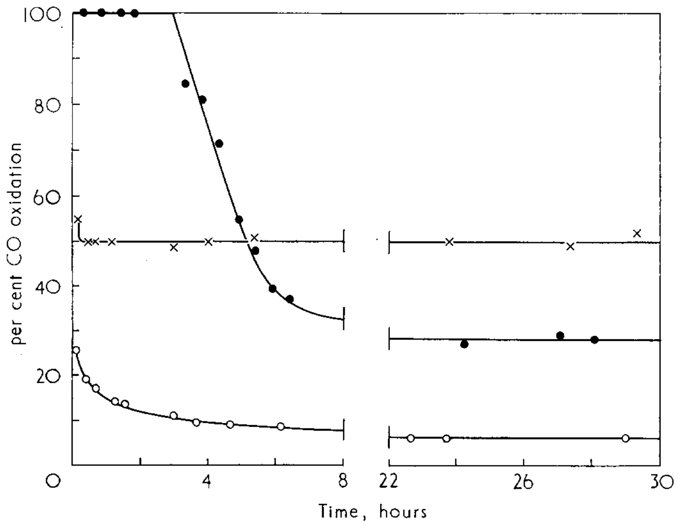

FIG. 3. Deactivation curves for calcined SnO_2 gels. 5.5% CO in air feed through 1.0 g SnO_2 beds at flow rate of 95 cm^3 min^{-1}. (—●—), reaction at 200°C on 450°C-calcined; (—×—), reaction at 200°C on 210°C-calcined; and (—○—), reaction at 150° on 210°C-calcined gel.

m^2g^{-1}; water content = 3.5%) are discussed later.

Arrhenius plots for CO oxidation on SnO_2 gel calcined at 450°, for small temperature ranges between 100 and 230°C, showed that the apparent activation energy for the reaction increased approximately linearly with temperature, giving values of 8 and 19 kcal $mole^{-1}$ at 130 and 210°C, respectively.

The kinetics of the reaction were studied within the fairly narrow temperature range 180–210°C. Before conducting the kinetics experiments, possible diffusion effects were studied. The effect of external (mass transfer) diffusion was investigated at 200°C by subjecting (a) a 0.6 g and (b) a 3.0 g catalyst bed to varying flow rates of a 6.0% CO in air mixture at space velocities equal to or less than those contemplated being used in the kinetics studies. The plots of % oxidation vs reciprocal space velocity for each catalyst bed coincided, indicating that, at the high space velocities used below for the kinetics studies, mass transfer effects can be neglected.

The effect of internal (pore) diffusion was investigated, again at 200°C, by studying the oxidation of 3–6% CO in air mixtures, at constant space velocity, on 0.3 g beds of (a) 20–36 and (b) 36–72 B.S.S. mesh catalyst granules. Plots of reaction rate vs feed CO concentration for each catalyst bed agreed well, indicating that pore diffusion effects can be ignored.

At 200°C the rate of oxidation of CO on SnO_2 gel calcined at 450°C is independent of both O_2 and CO_2 concentrations, as shown in Figs. 4 and 5, respectively. The O_2 and CO_2 dependences were studied using feeds of CO–N_2–air and CO–CO_2–air, respectively, at constant space velocities and constant CO concentrations.

The effect of CO concentration on the rate of reaction at 180, 190, 200, and 210°C is shown in Fig. 6. Because of the small catalyst bed used for this study, it was assumed that the pressure drop across the bed was negligible, and the p_{CO} values were calculated from measurements of the pressure in the reactor above the catalyst bed. The experimental points shown in Fig. 6 correspond to oxidations of between 2 and 20%.

These kinetic data for the oxidation of CO on SnO_2 gel activated at 450°C are qualitatively similar to those obtained for this reaction on both V_2O_5 (*11*) and Fe_2O_3 deposited on an alumina–silica support

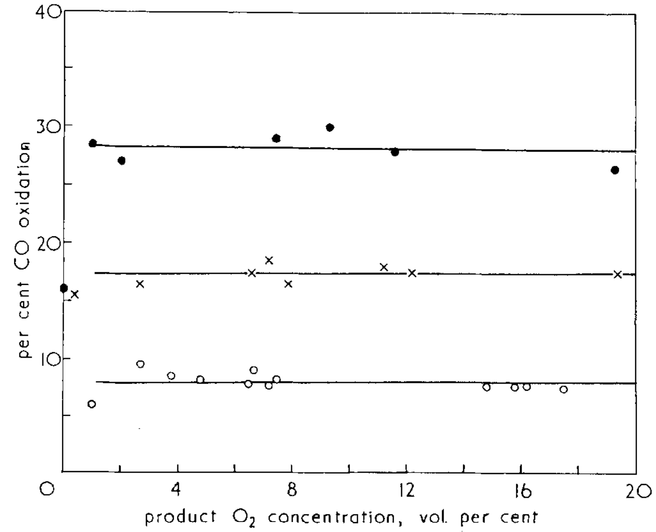

FIG. 4. Effect of O_2 concentration on rate of CO oxidation at 200°C on SnO_2 gel calcined at 450°. 5.5% CO in air feed at flow rates of: (—●—), 96 cm^3 min^{-1} through 1.0 g bed; (—×—), 200 cm^3 min^{-1} through 1.0 g bed; and (—○—), 98 cm^3 min^{-1} through 0.3 g bed.

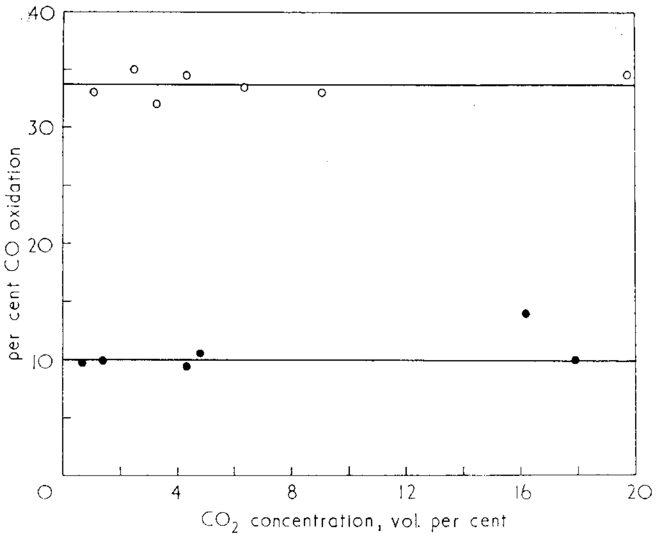

FIG. 5. Effect of CO_2 concentration on rate of CO oxidation at 200°C on SnO_2 gel calcined at 450°C. (—○—), 5.9% CO in feed at flow rate of 92 cm^3 min^{-1} through 1.5 g bed; (—●—), 10.7% CO in feed at flow rate of 98 cm^3 min^{-1} through 0.5 g bed.

(*12*), although SnO_2 is active at temperatures considerably lower than those of the other two catalysts.

These data can be satisfactorily explained by the following steady state reaction sequence:

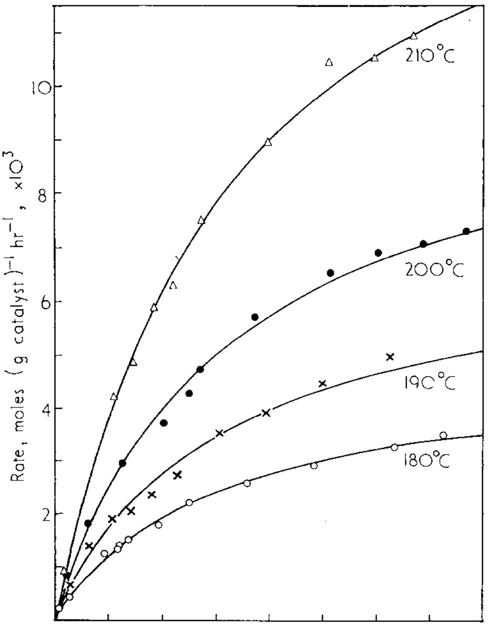

FIG. 6. Effect of CO concentration on rate of CO oxidation on SnO_2 gel calcined at 450°. Feed flow rates of 96–102 cm^3 min^{-1} through 0.3 g bed.

$$(OSnO) + CO \xrightarrow{k_1} (OSnOCO), \tag{1}$$

$$(OSnOCO) \xrightarrow{k_2} (OSn) + CO_2, \tag{2}$$

$$(OSn) + \tfrac{1}{2}O_2 \xrightarrow{\text{fast}} (OSnO), \tag{3}$$

where parentheses represent surface species, and k_1 and k_2 are rate constants.

Since the reaction rate is independent of both CO_2 and O_2 concentrations, Step (2) is irreversible and Step (3) fast.

Application of a Langmuir-type rate equation to the above mechanism gives (*11*):

$$R = \frac{k^1 k_1 p_{CO}}{1 + (k_1/k_2)p_{CO}} = \frac{A p_{CO}}{1 + B p_{CO}}, \tag{4}$$

where R is the reaction rate and k^1 a constant to allow for the fractional decomposition of (OSnOCO) sites at any instant, and also to convert the fractional surface coverage to a surface concentration.

Values of A and B for the results given in Fig. 6 were obtained from the best visual or least squares fit to the linear forms of Eq. (4):

$$R/p_{CO} = A - BR \tag{5}$$

and

$$1/R = 1/Ap_{CO} + B/A. \quad (6)$$

The mean values of A and B obtained by these methods are given in Table 1, and the curves shown in Fig. 6 are the theoretical ones obtained using these values.

TABLE 1
VALUES OF CONSTANTS A AND B IN EQ. (4)

Temperature °C	A, moles (g catalyst)$^{-1}$ (mm Hg)$^{-1}$hr^{-1} $\times 10^5$	B, (mm Hg)$^{-1}$ $\times 10^2$
180	8.12	1.68
190	11.40	1.62
200	16.43	1.61
210	25.31	1.57

The rate constants can be expressed in the form:

$$k_1 = Z_1 \exp(-E_1/RT) \quad (7)$$

and

$$k_2 = Z_2 \exp(-E_2/RT), \quad (8)$$

where E_1 and E_2 are the experimental activation energies (*13*) for the CO adsorption and CO_2 desorption stages, respectively; Z_1 and Z_2 are constants, assumed to be independent of the absolute temperature T.

Since $A = k^1k_1$ and $B = k_1/k_2$, it follows from Eqs. (7 and 8) that plots of $\log_{10}A$ and $\log_{10}B$ against $1/T$ should be linear with slopes of $-E_1/2.303\,R$ and $-(E_1 - E_2)/2.303\,R$, respectively.

The slopes obtained from these plots gave values of

$$E_1 = 16.4 \text{ kcal mole}^{-1} \quad \text{and} \quad E_2 = 17.4 \text{ kcal mole}^{-1}.$$

DISCUSSION

The above interpretation of the kinetics data demands that the catalyst undergoes successive reduction and reoxidation during CO-oxidation catalysis and, since the reaction on the steady state catalyst is independent of oxygen concentration, the reoxidation step at equilibrium must be considerably faster than the other two steps. The darkening in color of the catalyst during the partial deactivation to a steady state condition at low temperatures, however, is indicative of an overall partial reduction of the catalyst. Yoneda and Makishima (*5*) also observed this darkening and attributed it to a partial reduction.

Good evidence that the color changes are due to reduction by abstraction of oxygen from the SnO_2 was afforded by observing the effect of passing a CO–nitrogen feed through a catalyst bed preactivated in air at 450°C, and then held in an oxygen-free nitrogen stream at 450°C for 16 hr. It was assumed that this pretreatment would produce a surface free from chemisorbed oxygen. Upon introducing the CO at 200°C the catalyst rapidly turned black, the black color moving through the catalyst bed with a fairly sharp front. Chromatographic monitoring of the product gas clearly showed evolution of CO_2 (see Fig. 7), which broke through coincident with breakthrough of the black band. The CO_2 was evolved as a peak with a concentration equal to that of the feed CO concentration, after which it was desorbed as an extensive tail. After 4 hr, under the conditions quoted in Fig. 7, the amount of CO_2 being evolved was very small, and at this stage a total of 9.0 cm^3 of CO_2/g of catalyst had been desorbed. These results indicate that the chemisorbed CO is desorbed as CO_2 by a mechanism of lattice–oxygen abstraction. A similar irreversible chemisorption of CO has been observed at 200°C on other oxides, e.g., Cr_2O_3 (*14*) and NiO (*15*).

The above CO_2 desorption data indicate a composition for the partially reduced catalyst of $SnO_{1.94}$, assuming that the catalyst was initially stoichiometric SnO_2, and chemical analysis gave good agreement with this value. It was calculated that, for this catalyst (S = 36 m^{2}g^{-1}), the reduction can be accounted for by a mechanism of surface oxygen abstraction, and does not necessarily demand participation of bulk oxygen. The X-ray powder diffraction pattern and the transmission

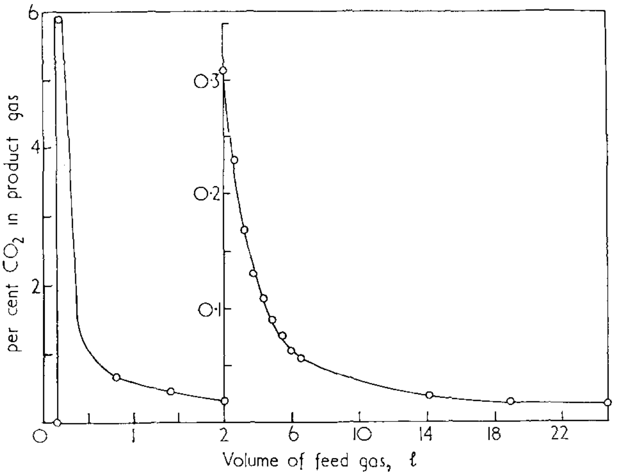

FIG. 7. The partial reduction of SnO_2 (calcined at 450°) by CO at 200°. 5.9% CO in N_2 feed at flow rate of 100 cm^3 min^{-1} through 3.0 g bed.

ir spectrum of the partially reduced SnO_2 were identical with those of the original material.

Visual comparisons of the above partially reduced, black SnO_2 with the steady state catalysts obtained in CO–air mixtures suggested that the degree of reduction in the latter cases is less. Accurate chemical analyses of the steady state catalysts were difficult because of the low degree of reduction, but these indicated that, even in the most extensively deactivated cases, the composition was $SnO_{>1.99}$. The wide variation in the colors of the steady state catalysts (i.e., pale brown to brown–black) suggests that these exist in varying degrees of reduction depending on the experimental conditions, in particular the calcination temperature of the gel and the reaction temperature during the CO oxidation. The fact that, at the same operating temperature, SnO_2 gel activated at higher temperatures (within the range 200–500°C) yields darker steady state catalysts suggests that the partially hydrated SnO_2 surface is less prone to reduction, and thus deactivates relatively less strongly than an essentially anhydrous surface. It was, in fact, found that SnO_2 gel activated at 210°C, although being initially far less active for CO oxidation than the material freshly activated at 450°C, gave, under comparable conditions at 180–200°C, a steady state reaction rate per unit weight of catalyst of about twice that of the high-temperature calcined material.

In view of the above observations it is surprising to find a zero oxygen dependence for CO oxidation under steady state conditions. This is shown in Fig. 4 for the 450°C activated material, and was also found to apply to the 210°C calcined product. Numerous other oxygen-dependence studies, in addition to those shown in Fig. 4, were undertaken, but in no instances was a significant (i.e., rate $\propto p_{O_2}^{>0.1}$) dependence observed. This suggests that the degree of reduction of the steady state catalysts in CO–air mixtures is independent of oxygen concentration provided that there is at least sufficient present to satisfy the CO oxidation. Confirmation of the stability of the steady state catalyst in an oxygen-containing atmosphere was obtained by subjecting the catalyst, activated at 450°C and equilibrated to steady state in CO–air at 200°C, to an air stream at 200°C. During passage of the air a marked desorption of CO_2 occurred [Fig. 8(○)], and at stage A no change in the brown–black color of the catalyst was observed, although a rapid reoxidation to a yellow–orange color occurred on heating in air to 350°C. An independent experiment showed that, upon reintroducing CO–air to the catalyst at stage A, a rapid return to steady state was achieved. If, however, the steady state catalyst were subjected to an air stream at 200°C for longer periods, a gradual reoxidation occurred, as indicated by a lightening in color of the catalyst. In this case some reactivation of the catalyst occurred, which required several hours to reestablish steady state in CO–air.

Our kinetics results are at variance with those of Yoneda and Makishima (*5*), who obtained an expression:

$$\text{Rate} \propto p_{CO}p_{O_2}^{0.25}$$

for SnO_2 gel calcined at 350°C and operated at 170°C. Although the above Langmuir rate Eq. (4) reduces to first order in p_{CO} for p_{CO} values below about 10 mm Hg, we have not been able to establish a significant oxygen dependence.

Yoneda and Makishima used a 0.3 g sample of catalyst and followed the reaction in a race-track type reactor by measuring pressure changes accompanying the oxidation. They found that the reaction required an induction period of about 8–12 min (depending upon whether O_2 or CO was in excess) and attributed this to reduction of the catalyst to steady state conditions. The kinetics equation was based on data obtained for about one hour after this induction period.

Our deactivation studies have shown, however, that a 0.3 g bed of SnO_2 gel activated at 350°C requires at least 5 hr to attain steady state at 170°C in a 6% CO in air mixture at a space velocity of ~20,000 hr^{-1}. The steady state catalyst is brown–black compared with the yellow–brown color observed by Yoneda and Makishima, which suggests the possibility that these workers were not investigating the steady state catalyst. It is probable, however, that the rate of attainment of steady state conditions is oxygen dependent, as indicated by the fact that partial reduction of SnO_2 by CO occurs very rapidly in the absence of oxygen. If this is so, then the activity of the catalyst at any stage before attainment of steady state will show an oxygen dependence.

The other interesting feature of these studies is the higher experimental activation energy for the CO_2 desorption step compared with that for CO adsorption. This indicates that the desorption step is considerably more rate determining on SnO_2 than on both V_2O_5 (*11*) and Fe_2O_3 (*12*). Figure 8 clearly shows that CO_2 can be desorbed from the steady state catalysts preactivated at both 210 and 450°C.

In conclusion, it has been shown that freshly activated SnO_2 gel is active at low temperatures for the catalytic oxidation of

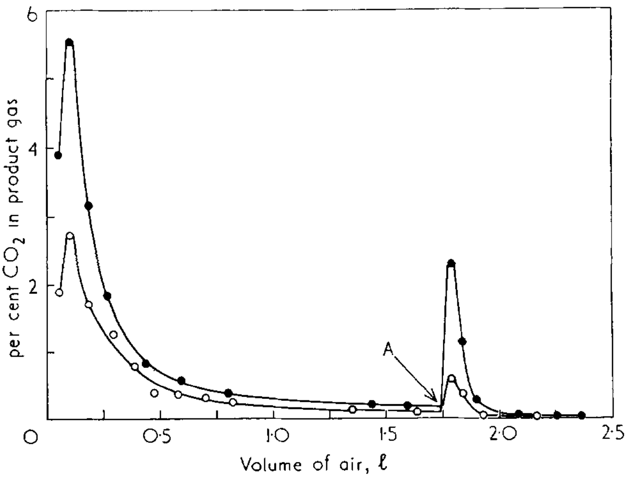

FIG. 8. Desorption of CO_2 from steady state SnO_2 catalysts. 4.5 g samples of catalyst equilibrated to steady state at 200°C in 6.0% CO–air, then flushed with air at 200°C at flow rate of 8 $cm^3\ min^{-1}$. (—●—), 210°C- and (—○—), 450°C-calcined gel. At stage A temperature was increased to 350°C.

CO, and even after partial deactivation to steady state conditions it is active for this reaction at temperatures considerably lower than those for most other n-type oxides. A similar unexpectedly high activity has been observed for the catalytic decomposition of nitrous oxide on SnO_2 (*16*).

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