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The Catalytic Oxidation of Carbon Monoxide on SnO_2–CuO Gels

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Coprecipitated SnO_2–CuO gels are active catalysts for the low-temperature (ambient–100°C) steady state oxidation of carbon monoxide after thermal activation at temperatures up to 450°C. Using the described method of preparation maximum catalytic activity occurs at a Cu:Sn atomic ratio of ~0.55:1, and evidence from pH-titration, thermal analysis, and X-ray data suggests that this activity is a consequence of the ion-exchange sorption of Cu(II) ions on the surface of primary hydrous SnO_2 particles formed during the precipitation process. X-Ray data on SnO_2–CuO gels show no evidence for the formation of a mixed oxide compound or solid solution after calcination at temperatures up to 1000°C.

Steady state CO oxidation at 70°C on 450°C-activated $SnO_2\cdot 0.55CuO$ obeys the empirical rate equation:

$$\frac{d(CO_2)}{dt} \propto \frac{p_{CO}{}^{0.43} p_{O_2}{}^{0.10}}{p_{CO_2}{}^{0.37}}.$$

INTRODUCTION

We have previously shown (*1*) that catalysts produced by the thermal activation of hydrous SnO_2 gel in the temperature range 200–500°C are active for CO oxidation at moderately low temperatures (<200°C). Subsequently we have studied the effect on CO-oxidation activity of coprecipitating hydrous SnO_2 with 11 other oxides [i.e., those of Al(III), V(V), Cr(III), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ce(III), and U(VI)]. For preliminary comparative experiments SnO_2–M_xO_y gels were prepared at a M:Sn atomic ratio of ~0.1:1, activated at 450°C in dry air, and tested for steady state CO-oxidation activity at 180°C.

Although some of the catalysts, notably those containing uranium, iron or cerium, showed an increase in catalytic activity (on a rate per unit weight basis) compared with SnO_2, the activity of the SnO_2–CuO coprecipitate, using this basis of comparison, was at least an order of magnitude better than any of the other catalysts.

We have previously briefly reported (*2*) that SnO_2–CuO gels, particularly those having a Cu:Sn atomic ratio of between 0.5:1 and 0.6:1, are active catalysts for the low-temperature (<100°C) oxidation of CO, and a comparison of the CO-oxidation activity of a catalyst of composition $SnO_2\cdot 0.53CuO$ with both a commercial hopcalite and SnO_2 has been made. In this paper we report, in more detail, results of physicochemical and catalytic studies on SnO_2–CuO gels of varying compositions.

METHODS

Preparation of the Catalysts

The catalysts were precipitated by the dropwise addition of AnalaR concentrated aqueous NH_3 to well-stirred solutions of 0.1 *M* [$SnCl_4 + Cu(NO_3)_2$] to pH 7.0 ± 0.1. The precipitates were repeatedly centrifuged and redispersed in distilled water until peptization was imminent, then again centrifuged and allowed to dry in air at ambient temperature. The dried gel granules were then column washed over several days with water, again followed by air drying at ambient temperature. Materials prepared with Cu:Sn atomic ratios ⩽0.7:1

were typical glassy dried gel materials, whereas preparations with higher copper contents yielded opaque granules.

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.

Catalytic Studies and Gas Analyses

The catalytic apparatus and gases used, and the methods of volumetric and chromatographic gas analyses were as previously reported (*1*), with the exception that CO_2 rate-dependence determinations were calculated from differences in the feed and product CO concentrations obtained by chromatographing on a molecular sieve type 5A column at 100°C.

As was previously observed for SnO_2 (*1*), freshly activated SnO_2–CuO gels were found to have considerably higher CO-oxidation activities than the steady state catalysts (see below), obtained after equilibrating the catalysts with the reactant gases at the required temperature. Unless otherwise stated, all catalysis data presented refer to the steady state condition. At the reaction temperatures ($\leqslant 100°C$) and reactant concentrations and feed rates (typically 5% CO in air at 100 $cm^3\ min^{-1}$) used, the time required for attainment of steady state varied from about 16 hr (for <0.5 g catalyst beds) to about 40 hr (for 3–6 g beds). In all instances the steady state catalysts returned to their higher initial activities after thermal reactivation in air.

Physical and Chemical Characterization

Specific surface area determinations and X-ray powder diffraction data were obtained as previously described (*1*).

Simultaneous thermogravimetry (TG) and differential thermal analyses (DTA) were obtained using a Stanton TR-02 thermobalance with a Stanton 661 DTA attachment employing alumina as the DTA reference material.

The tin contents of the catalysts were obtained by digesting with hot 8 *M* HNO_3, to extract the copper, followed by dilution, hot filtration of the insoluble "stannic acid," washing with 0.2 *M* HNO_3, calcining, and weighing as SnO_2.

The copper contents were determined by volatilizing tin as $SnBr_4$ from the catalysts using 10% Br_2 in HBr (sp gr 1.48) followed by iodimetric titration of copper in the residue with thiosulfate solution.

Results and Discussion

Figure 1 shows the effect of the composition of SnO_2–CuO gels, after activation at 450°C, on their CO-oxidation activities at 100°C and on their BET specific surface areas. The figure clearly shows that the increase in catalytic activity conferred on SnO_2 by coprecipitation with Cu(II) passes through a maximum (both on a unit weight and unit surface area basis) at a Cu:Sn ratio of approximately 0.55:1, indicating that the catalytic activity cannot be ascribed to the presence of active CuO on an inactive SnO_2 support. Further confirmation of the active participation of tin in the SnO_2–CuO gels was obtained by assessing the catalytic activities for CO

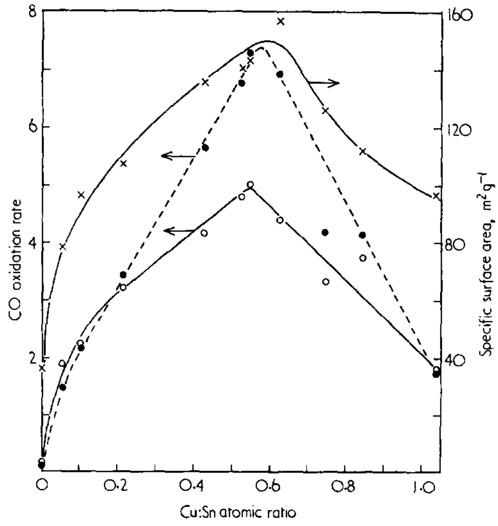


FIG. 1. Effect of composition of 450°C-activated SnO_2–CuO gels on their CO-oxidation activities at 100°C and their BET specific surface areas. Rates quoted for 0.2 g catalyst beds and mean p_{CO} 40 mm Hg using CO–air feed rates of 100 ± 2 $cm^3\ min^{-1}$. Rate units: (●--) moles CO_2 (g catalyst)$^{-1}$ hr^{-1} × 10^3; (○—) moles CO_2 m^{-2} hr^{-1} × 10^5.

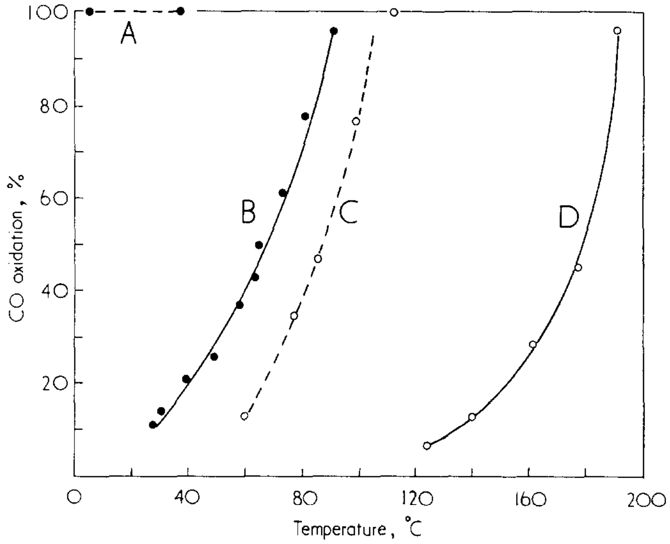


FIG. 2. Oxidation of 5–6% CO in air at flow rate of 100 ± 2 cm^3 min^{-1} through 3.0 cm^3 beds of 450°C-activated catalysts. (●) SnO_2·0.53CuO (6.0 g): (A) initial activity; (B) steady state; (○) SnO_2 (7.4 g): (C) initial activity; (D) steady state.

oxidation of similarly prepared Al_2O_3–CuO gels. These had specific surface areas (100–200 m^2 g^{-1}) comparable with those of the SnO_2–CuO gels, but were found to have negligible CO-oxidation activity for temperatures up to at least 100°C.

The low-temperature CO-oxidation activity of a catalyst of composition SnO_2·0.53CuO is illustrated in Fig. 2, which also shows, for comparison, data for SnO_2 gel. Values of initial activities were obtained exactly 30 min after thermal activation. Steady state data were obtained for increasing-temperature steps after allowing

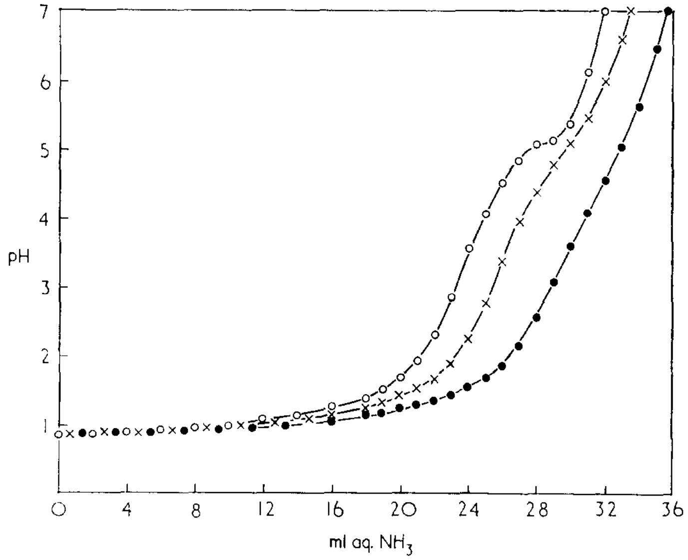


FIG. 3. pH-titration curves for the hydrolysis of 1.5 liters 0.1 *M* [$SnCl_4$ + $Cu(NO_3)_2$] solutions with concentrated aqueous NH_3. Cu:Sn atomic ratios: (●—) 0.43:1; (×—) 0.63:1; (○—) 0.84:1.

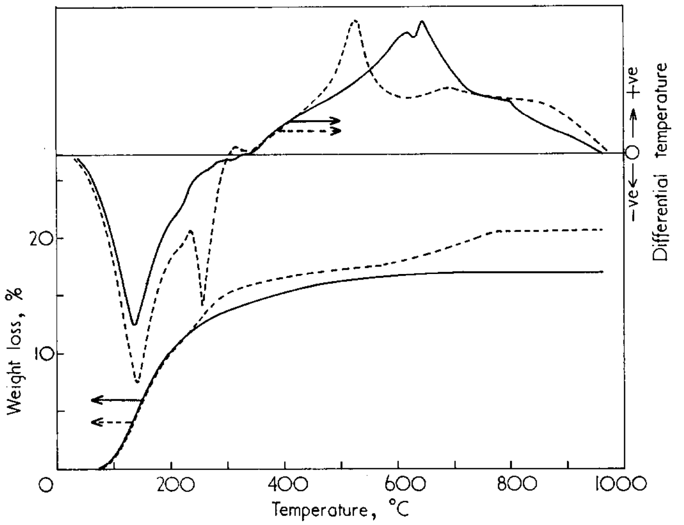


FIG. 4. TG–DTA curves. (—) Hydrous SnO_2·0.55CuO gel; (- - -) hydrous SnO_2·1.03CuO gel; heating rate, 6°C min^{-1}.

the catalysts to equilibrate for ~40 hr at temperatures which gave steady state oxidations of between 5 and 20%. It is apparent that the freshly activated SnO_2–CuO catalyst is very active at temperatures below ambient and even after equilibration to steady state it still shows some room temperature activity. An Arrhenius plot for the steady state data for the SnO_2·0.53CuO catalyst gave an apparent activation energy for the reaction of 7.5 kcal mole^{-1} at 30–80°C.

Physicochemical studies were undertaken in an attempt to establish the reason for the effect of the composition of SnO_2–CuO gels on their catalytic behavior. pH-titration curves for the coprecipitation of three of the SnO_2–CuO preparations are shown in Fig. 3, and Fig. 4 shows the TG–DTA curves for the optimum catalyst (SnO_2·0.55CuO) and a higher copper content catalyst (SnO_2·1.03CuO). Table 1 summarizes the X-ray powder diffraction data obtained for the calcined catalysts, and Fig. 5 shows the effect of calcination temperature on the BET specific surface area and catalytic activity at 100°C of the optimum catalyst.

It is convenient to discuss the structure–activity relationship of the SnO_2–CuO catalysts for calcination temperatures (i) up to 450°C and (ii) above 450°C.

TABLE 1
X-RAY POWDER DIFFRACTION DATA FOR CALCINED SnO_2–CuO GELS

Calcination temp (°C)	Catalyst composition	
	Cu:Sn < 0.6:1	Cu:Sn > 0.6:1
450	Only SnO_2 phase detected, lines becoming increasingly weak and broad with increasing Cu content	Very weak and broad SnO_2 pattern Sharp CuO pattern
450–1000	Two component SnO_2 + CuO systems, increasing in crystallinity with increasing calcination temperature	

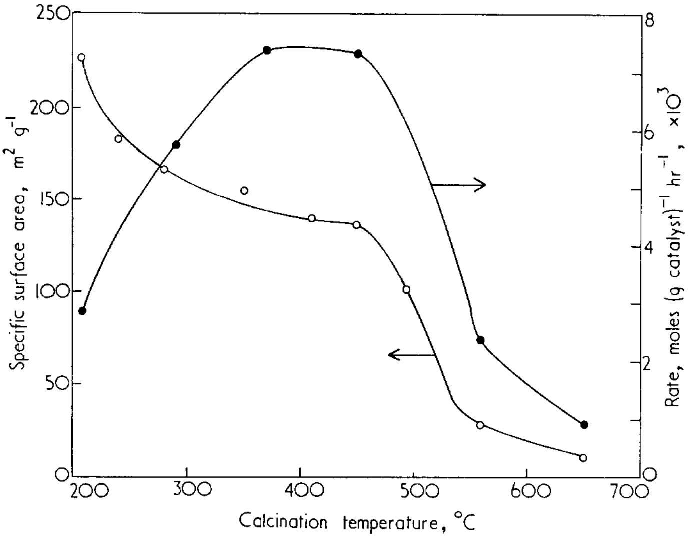
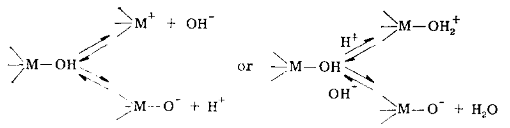


FIG. 5. Effect of calcination temperature of the BET specific surface area and CO-oxidation activity at 100°C of $SnO_2 \cdot 0.55CuO$. Rate data obtained as for Fig. 1.

Structure of SnO_2–CuO Gels in Relation to Catalytic Activity for Calcination Temperatures up to 450°C

The pH-titration curves (Fig. 3) all clearly show the Sn(IV) hydrolysis plateau for precipitation of hydrous SnO_2 at pH 1.2 to 1.3. However, only for Cu:Sn atomic ratios above about 0.6:1 did an inflection point at pH 5.2 due to the precipitation of free $Cu(OH)_2$ become evident.

This behavior can be attributed to the ion-exchange properties of hydrous SnO_2. The ion-exchange properties of hydrous oxides in general (*3*, *4*) and hydrous SnO_2 in particular (*5*) have been extensively studied and reviewed. In the case of an amphoteric hydrous oxide, such as hydrous SnO_2, ion-exchange behavior can be attributed to the amphoteric reactions of hydroxyl groups:



The upper reactions, producing anion-exchange properties, are favored by low pH, whereas the lower reactions, which are favored by high pH, result in cation-exchange characteristics.

During the slow addition of aqueous NH_3 to a solution of $SnCl_4 + Cu(NO_3)_2$, hydrolysis of Sn(IV) occurs, and precipitation of hydrous SnO_2 begins at pH 1.2–1.3. At this low pH only little ion-exchange sorption of Cu(II) occurs, and an independent preparation for a Cu:Sn solution atomic ratio of 1:1 showed that, after arresting the NH_3 addition at pH 1.5, the composition of the precipitate was $SnO_2 \cdot 0.05CuO$. However, upon increasing the pH from 1.5 to 5.0 the Cu(II) begins to ion exchange extensively on the hydrous SnO_2 particles. If there is insufficient Cu(II) present in solution to satisfy the ion-exchange capacity of the hydrous SnO_2 for Cu(II) at pH 5 then this species is completely ion exchanged. When the Cu(II) content of the solution exceeds this ion-exchange capacity, then the excess is precipitated as $Cu(OH)_2$ at pH ~5.2.

A comparison of Figs. 1 and 3 indicates that maximum catalytic activity of 450°C-activated SnO_2–CuO gels corresponds approximately with maximum uptake of Cu(II) by ion exchange. For Cu:Sn ratios below about 0.6:1 the catalysts may be viewed, at least in the room temperature dried form, as Cu(II) sorbed by ion-exchange on SnO_2 and in this form the Cu(II) is readily eluted from the supporting SnO_2 gel with, e.g., dilute HNO_3. The pH titration data indicate, in addition to ion exchange, the precipitation of free $Cu(OH)_2$ for copper contents above this.

This is clearly evident from the ambient–450°C TG–DTA data (Fig. 4). In the case of the optimum composition catalyst ($SnO_2 \cdot 0.55CuO$) the weight loss due to dehydration is a single stage process with an endothermic DTA peak at 137°C at the heating rate employed. The high copper content gel, however, shows a further endothermic dehydration step with a peak at 258°C, attributable to the dehydration of free $Cu(OH)_2$.

The X-ray diffraction data for the SnO_2–CuO gels calcined at 450°C (Table 1) also clearly indicated the presence of well-defined crystalline CuO in the catalysts with Cu:Sn ratios above about 0.6:1, whereas at lower Cu contents the only crystalline phase observed was that of SnO_2.

One interesting consequence of the ion-exchange sorption of Cu(II) onto hydrous SnO_2 is the resistance to thermal sintering of the SnO_2–CuO gels when calcined at temperatures up to 450°C. Table 1 indicates that the crystal growth of SnO_2 decreases with increasing amounts of ion-exchanged Cu(II), and Fig. 1 shows how this is reflected in the specific surface areas of 450°C-calcined catalysts. The decrease in specific surface area for catalysts with high copper contents is probably due to (i) the crystallization of the free CuO to, presumably, low specific surface area material, and (ii) a pore-blocking effect of this free CuO. Figure 5 shows the absence of a marked decrease in specific surface area of the optimum composition catalyst for calcination temperatures between 300 and 400°C, as was observed for hydrous SnO_2 (*1*). The increase in catalytic activity with increasing activation temperature between 200 and 400°C is presumably due to more extensive dehydration of the catalyst surface.

Resistance towards thermal sintering at 450°C was found to be general for the ion-exchange coprecipitation of a number of elements [e.g., Al(III), V(V), Cr(III), Cr(VI), Mn(II), Fe(III), Co(II), Ni(II), Ce(III), and U(VI)] with hydrous SnO_2. The presence of the ion-exchanged phase on the surface of the hydrous SnO_2 particles apparently acts as a surface impurity, preventing crystallization of the SnO_2.

Structure of SnO_2–CuO Gels in Relation to Catalytic Activity for Calcination Temperatures Above 450°C

When calcined at temperatures above 450°C, SnO_2–CuO gels undergo marked changes in physical properties and catalytic activity. Even in gels which previously showed no evidence of free CuO on calcining at 450°C (i.e., Cu:Sn $< 0.6{:}1$), X-ray studies (Table 1) clearly showed the appearance of free CuO. This segregation and sintering of the catalysts into two-component (SnO_2 + CuO) crystalline systems resulted in a marked decrease in specific surface area, accompanied by a decrease in CO-oxidation activity (expressed on a unit weight basis) as shown in Fig. 5, although even after calcination at 650°C, $SnO_2 \cdot 0.55CuO$ still retains some CO-oxidation activity at 100°C.

DTA studies (Fig. 4) on both the optimum ($SnO_2 \cdot 0.55CuO$) and high ($SnO_2 \cdot 1.03CuO$) copper content gels showed the occurrence of exothermic reactions at temperatures between 450 and 700°C, presumably attributable to crystallization processes.

TG studies on the highest copper content catalysts (i.e., Cu:Sn $> 0.8{:}1$) also showed an additional weight loss at temperatures between 600 and 800°C at the heating rate used (see Fig. 4). This was observed as a white sublimate on heating these catalysts at $\geqslant$450°C in a stream of argon, and the X-ray powder diffraction pattern identified it as Cu_2Cl_2. Thus, even after extensive washing, these high copper content catalysts still retain residual chloride ions. However, the decrease in catalytic activity of the high copper content catalysts cannot be ascribed to the presence of chloride since sublimation, on heating, was not observed for Cu:Sn ratios below 0.8:1, whereas catalytic activity began to de-

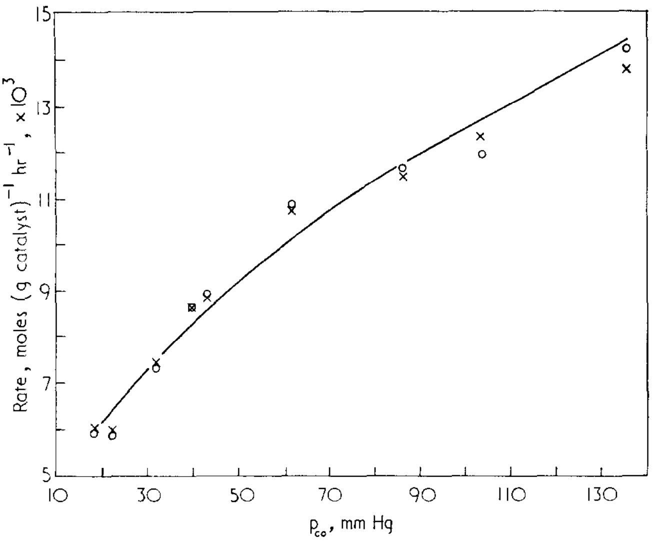


FIG. 6. Effect of CO concentration on rate of CO oxidation on 450°C-activated $SnO_2 \cdot 0.55CuO$. Feed flow rates of 100 ± 2 cm^3 min^{-1} through 3.0 g bed. (×) Experimental points obtained for p_{O_2} in the range 144–163 mm Hg and p_{CO_2} in the range 9.8–12.4 mm Hg; (○) points corrected for p_{O_2} 156 mm Hg and p_{CO_2} 10.8 mm Hg.

crease for catalysts with Cu:Sn ratios above ~0.55:1.

Kinetics Studies

The kinetics of CO oxidation on 450°C-activated $SnO_2 \cdot 0.55CuO$ were studied at 70°C. At this temperature the rate of reaction is dependent on the concentrations of all three components, as shown in Figs. 6–8. CO, CO_2, and O_2 dependences were studied using feeds of CO–0.9% CO_2 in air, CO–CO_2–air and CO–N_2–air, respectively.

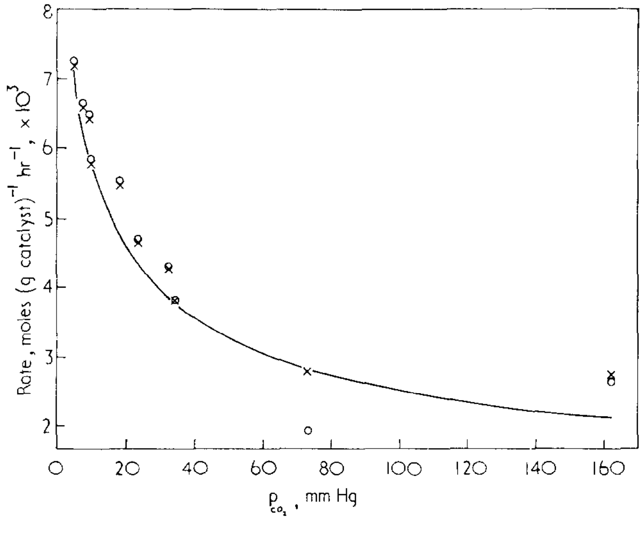


FIG. 7. Effect of CO_2 concentration on rate of CO oxidation on 450°C-activated $SnO_2 \cdot 0.55CuO$. Feed flow rates of 100 ± 2 cm^3 min^{-1} through 3.0 g bed. (×) Experimental points obtained for p_{CO} in the range 31.7–36.5 mm Hg and p_{O_2} in the range 119–152 mm Hg; (○) points corrected for p_{CO} 32.7 mm Hg and p_{O_2} 147 mm Hg.

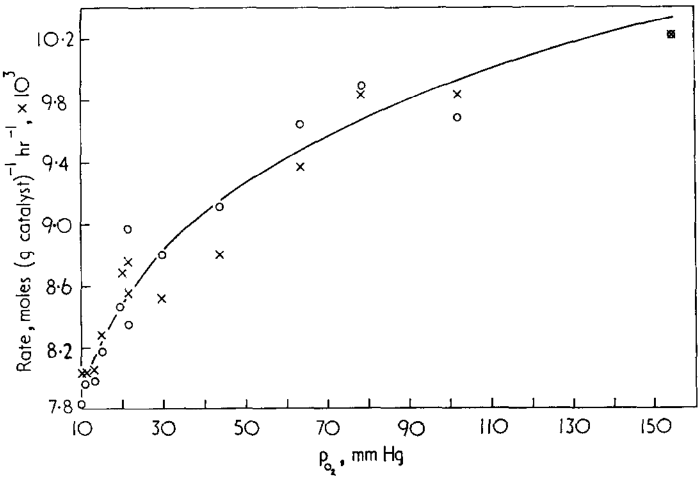


FIG. 8. Effect of O_2 concentration on rate of CO oxidation on 450°C-activated $SnO_2 \cdot 0.55CuO$. Feed flow rates of 100 ± 2 cm^3 min^{-1} through 3.0 g bed. (×) Experimental points obtained for p_{CO} in the range 38.6–44.9 mm Hg and p_{CO_2} in the range 3.7–5.0 mm Hg; (○) points corrected for p_{CO} 41.9 mm Hg and p_{CO_2} 4.1 mm Hg.

In most cases the relative changes in concentration of the reactants and added CO_2 upon passage through the catalyst bed were small, and the partial pressures of the gases quoted in the legends of Figs. 6–8 are the arithmetic mean of the feed and product partial pressures. One exception to this was in the oxygen-dependence studies, where CO_2 was not introduced in the feed gas stream. However, the dependence of the reaction rate on p_{O_2} was so small over the p_{O_2} range studied that the product p_{CO_2} was essentially constant, and thus the p_{CO_2} gradient through the catalyst bed was practically the same for all the oxygen-dependence results.

When studying the rate dependence of one of the components of the reaction, the partial pressures of the other two components were held essentially constant. In any case, corrections for the slight deviations from constancy were made, and the corrected values are shown in Figs. 6–8. The corrected rates for any one component were obtained by a series of approximations using the rate-dependence results of the other two components until self-consistency in the corrected rates was obtained. It is apparent from Figs. 6–8 that in no case do these corrections significantly alter the position or shape of the rate-dependence curve obtained for the experimental points.

From these results, an empirical rate expression for the reaction at 70°C can be established, viz,

$$\frac{d(CO_2)}{dt} \propto \frac{p_{CO}{}^{0.43} p_{O_2}{}^{0.10}}{p_{CO_2}{}^{0.37}}.$$

The curves shown in Figs. 6–8 are those obtained from the best linear fits to plots of log rate against 0.43 log p_{CO}, -0.37 log p_{CO_2}, and 0.10 log p_{O_2}, respectively.

One notable feature of the kinetics studies is the inhibition of the CO oxidation rate at 70°C by CO_2 (Fig. 7). This has also been observed for the low-temperature reaction on NiO (*6–9*) but, interestingly, not on Cu_2O (*6, 7*). Further chemisorption studies are in progress in an attempt to elucidate the reason for the CO_2 inhibition effect.

CONCLUSION

The high CO-oxidation activity of coprecipitated SnO_2–CuO gels, after calcination at temperatures up to 450°C, has been attributed to the ion-exchange sorption of Cu(II) on the surface of the primary hydrous SnO_2 particles formed during the precipitation process. Maximum catalytic activity occurs when the apparent cation-exchange capacity of the hydrous SnO_2 towards Cu(II) has been fully utilized. Using the described method of preparation, this occurs at a Cu:Sn atomic ratio of ~0.55:1, equivalent to 7.3 mEq Cu^{2+}/g SnO_2. For copper concentrations above this, formation of free $Cu(OH)_2$ occurs which, after thermal activation, decomposes to CuO. This has a detrimental effect on catalytic activity, both on a unit weight and unit surface area basis.

It is considered unlikely that the catalytic activity is significantly attributable to changes in bulk electronic properties due to the substitution of Cu^{2+} for Sn^{4+} in the bulk catalyst, even though ionic size considerations (both ions have an ionic radius of 0.72 Å) are favorable for this to occur. However, it is unlikely that this process could occur to the extent of 0.55 Cu^{2+} per Sn^{4+} without resulting in marked distortion of the SnO_2 lattice. If the catalytic activity were attributable to bulk ionic substitution, it would be expected to reach a maximum at a much lower Cu:Sn ratio. The only crystalline phases detected by X-ray diffraction after calcining SnO_2–CuO gels at temperatures up to 1000°C were those of SnO_2 (with no detectable lattice distortion) and CuO, and in no case was a crystalline phase attributable to the formation of a mixed tin oxide–copper oxide compound observed.

Current understanding of the mechanism of cation exchange on hydrous oxides predicts that surface groupings of the type $\equiv$Sn—O—Cu— would result from the ion-exchange sorption of Cu^{2+} on a hydrous SnO_2 precipitate. Whether the catalytic activity of the SnO_2–CuO gels is directly attributable to these groupings, or whether thermal activation results in some diffusion of the copper ions into the surface of the SnO_2 lattice is not, at present, clear. More detailed surface studies on these catalysts are required to elucidate this point. Nevertheless, the importance of initially bringing the Cu^{2+} ions to the surface of the SnO_2 by an ion-exchange process has been demonstrated.

When calcined at temperatures above 450°C the active surface is largely destroyed. Segregation into a two component (SnO_2 + CuO) system occurs, accompanied by a marked reduction in specific surface area of the catalysts due to crystallization, and a resultant decrease in catalytic activity.

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