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The Catalytic Reduction of Nitric Oxide by Carbon Monoxide over SnO_2–CuO Gels

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Coprecipitated SnO_2–CuO gels, after thermal activation at 200–500°C, are very active catalysts for the low-temperature (150°C) reduction of NO by CO, yielding both N_2O and N_2 as reduction products at this temperature. Maximum catalytic activity occurs at a Cu:Sn atomic ratio of $\sim$0.55:1, and structural arguments similar to those previously forwarded to explain the effect of catalyst composition on the CO-oxidation activities of these catalysts (Fuller, M. J., and Warwick, M. E., *J. Catal.* **34**, 445 (1974)) apply to the CO–NO reaction. During the reaction the catalyst exists in a surface-reduced state, and the formation of both N_2 and N_2O from NO appears to occur predominantly by a catalyst redox mechanism. The low-temperature ($<$150°C) reduction of N_2O by CO, the rate of which cannot be accounted for by a catalyst redox mechanism, is even more rapid than NO reduction but is inhibited by NO, thus explaining the presence of product N_2O during the low-temperature CO–NO reaction.

INTRODUCTION

The low-temperature catalytic reactions involving CO oxidation and the reduction of NO by CO have been extensively studied in recent years with a view to automobile exhaust purification.

We have previously reported (*1, 2*) that coprecipitated SnO_2–CuO gels, after thermal activation at temperatures between 200 and 450°C, are active catalysts for the low-temperature (ambient–100°C) oxidation of CO. Maximum catalytic activity was observed at a Cu:Sn atomic ratio of $\sim$0.55:1, and evidence was presented (*2*) which indicated 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. When the copper content of the solutions from which catalysts are precipitated exceeds this maximum ion-exchange uptake ratio, then the excess is precipitated as free $Cu(OH)_2$. This decomposes to CuO after thermal activation and has a detrimental effect on CO-oxidation activity on both a unit weight and unit surface area basis.

Subsequent studies have also shown that these SnO_2–CuO gels are very active for the low-temperature catalytic reduction of NO by CO, and we have briefly presented comparative results for this reaction at 150°C on $SnO_2\cdot$(0.51–0.55)CuO gels, SnO_2 gels, Al_2O_3–CuO gels, and a commercial barium-promoted copper chromite (Girdler G-22) catalyst (*3*). In addition, other workers (*4*) have recently shown that SnO_2 containing small amounts of Cr_2O_3 is also a very active catalyst for the reduction of NO by reducing gases.

Although the CO–NO reaction has been studied on a number of copper-containing catalysts (e.g., *5–18*), most mechanistic and kinetic studies have been undertaken on the commercial copper chromite catalysts (*7, 9, 10, 13, 16*). Using concentrations of up to 0.3% NO and up to 2% CO, the reaction is approximately first order in p_{NO} on these catalysts (*9*, *13*). Considerable quantities of N_2O, in addition to N_2, are produced, particularly at low temperatures (*9*, *11*, *13*), and Baker and Doerr (*9*) have postulated the low-temperature mechanism as involving reduction of the catalyst by CO, thus creating oxygen deficiencies, followed by stepwise catalyst reoxidation by NO to produce, first, N_2O, then N_2. The ability of copper chromite to undergo successive reduction–reoxidation during CO–NO cycling had previously been observed by other workers (*7*).

In contrast, Ayen and Ng (*10*), using CO and NO concentrations of up to 5% and temperatures of 160–240°C, and Force and Ayen (*16*), using concentrations and temperatures more characteristic of automobile exhaust, have postulated a catalyst dual-site reaction mechanism in which the rate-determining step is a surface reaction between two adjacently adsorbed CO and NO molecules.

In the present paper we report results of studies of the CO–NO reaction over SnO_2–CuO gels and, for comparison, other coprecipitated SnO_2–M_xO_y gels, where M = Mn(II), Al(III), Ce(III), Cr(III), Co(II), UO_2(II), Ni(II), or Fe(III). Some investigations have been undertaken in order to obtain mechanistic insight into the CO–NO reaction over SnO_2–CuO gels with particular emphasis on distinguishing between possible catalyst redox and dual-site contributions.

METHODS

Catalyst preparation and characterization. The preparation of the SnO_2–CuO gels of varying compositions has been described previously (*2*). Other SnO_2–M_xO_y (M:Sn atomic ratio = 0.1:1) gel granules used for a comparative activity study were prepared by a similar method, using either nitrates or chlorides of the metals M. At these low loadings a final pH of 4.5 (instead of 7.0) was found to be sufficient for complete ion-exchange coprecipitation with the hydrous SnO_2.

Specific surface area measurements (BET) and full nitrogen adsorption isotherms were obtained at −196°C using a conventional volumetric gas adsorption apparatus. X-ray powder diffraction data were obtained with Ni-filtered CuKα radiation (50 kV, 30 mA) using both photographic film (2–16-hr exposure) and diffractometer [$d(2\theta)/dt = 0.125° \text{ min}^{-1}$] methods.

Catalytic studies and gas analyses. The apparatus used to obtain the steady-state catalysis data (*19*) and the "microreactor" (*20*) used for some of the experiments were as previously reported.

Activated molecular sieve type 5A pellets were used exclusively for drying the feed gases, and the NO ($\geqslant$99%) was supplied by Matheson.

Throughout, 36–72 B.S.S. mesh catalyst granules were used, and thermal pretreatment was for 18 hr at the required temperature. All catalysis data quoted, except those in the Mechanistic Studies section, refer to the reaction after 6 hr (essentially steady state).

The reactant and product gases were separated and analyzed by chromatographing on a molecular sieve type 5A column (Perkin–Elmer F 11 gas chromatograph, hot wire detectors, and He carrier gas) at 100°C (for N_2, NO, and CO) followed by programming to 350°C (for N_2O and CO_2). CO_2 concentrations could not be quantitatively determined from this column and, where required, were determined separately on a Porapak Q column at 50°C. This column also permitted an alternative, more rapid analysis for N_2O.

RESULTS AND DISCUSSION

Table 1 shows the results of a comparative study of the activities for the CO–NO reaction at 200°C of an SnO_2 gel and a series of SnO_2–M_xO_y gels (M:Sn atomic

TABLE 1

Catalytic Reduction at 200°C of NO by CO over SnO_2 and Coprecipitated SnO_2–M_xO_y Gels (M:Sn = 0.1:1)[a]

Species M	S_{BET}^{N} (m^2g^{-1})	NO reduction (%)		
		To N_2	To N_2O	Total
None	36	5.1	7.4	12.5
Mn(II)	82	2.7	3.4	6.1
Al(III)	113	6.3	7.3	13.6
Ce(III)	80	7.2	6.5	13.7
Cr(III)	113	5.0	11.2	16.2
Co(II)	114	5.6	19.6	25.2
UO_2(II)	98	15.8	32.0	47.8
Ni(II)	87	8.0	40.5	48.5
Fe(III)	110	5.2	54.2	59.4
Cu(II)	98	83.5	5.3	88.8

[a] Feed of 14–15 vol% NO in CO at flow rate of 30 cm^3 min^{-1} through 1.0-g beds of 450°C-activated catalysts.

ratio = 0.1:1). The oxidation states quoted for the species M are those in the salts used for the coprecipitation. Different oxidation states might well result in certain cases after thermal activation or, in particular, after use under the overall reducing conditions encountered during the CO–NO reaction. Apart from X-ray diffraction studies, which showed only the SnO_2 crystalline phase in all cases, attempts have not been made to identify these valency states.

If expressed on an activity per unit surface area basis, it would appear that coprecipitation of SnO_2 with Mn(II), Al(III), Ce(III), Cr(III), and Co(II) has a deleterious effect on catalytic activity compared with SnO_2 alone. UO_2(II), Ni(II), and Fe(III) result in enhanced activities, although, at the temperature employed, selectively for the partial reduction of N_2O predominates. The superiority of the SnO_2–CuO gel, both for NO conversion and N_2 selectivity, is apparent.

Figure 1 shows the effect of chemical composition of the SnO_2–CuO gels on their catalytic activity at 150°C for the reduction of NO by CO. The specific surface areas of these catalysts after activation at 450°C have been reported previously (*2*). Although the total NO conversion is little changed over quite a wide catalyst composition range (i.e., Cu:Sn between 0.2:1 and 0.6:1), the value of comparing catalytic activities for conversions in excess of 80% is questionable. However, it is obvious from the figure that the catalyst composition has a marked effect on selectivity for the complete reduction to N_2. Maximum selectivity for this reaction occurs at a catalyst Cu:Sn composition of ~0.55:1 on both a unit weight and unit surface area basis (the latter is not illustrated in Fig. 1 to avoid congestion). This is the same catalyst composition where maximum CO-oxidation activity has been observed on these gels, and the significance of this composition coinciding with the maximum extent of ion-exchange uptake of Cu(II) ions by hydrous SnO_2 without precipitation of free $Cu(OH)_2$ has been discussed in detail (*2*). The decrease in catalytic activity at Cu:Sn ratios above ~0.6:1, coinciding with the presence of free CuO after thermal activation, is very extensive and far more marked than that previously observed for CO oxidation.

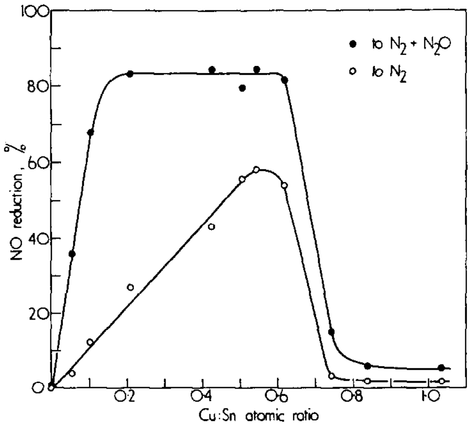

FIG. 1. Effect of composition of 450°C-activated SnO_2–CuO gels on their activity for the reduction of NO by CO at 150°C. Feed of 14–15% NO in CO at 30 cm^3 min^{-1} through 1.0-g beds.

From physicochemical arguments similar to those previously discussed for the SnO_2–CuO gels (*2*), the SnO_2–M_xO_y gels, at least for M : Sn ratios of 0.1 : 1, may also be viewed as hydrous SnO_2 containing the coprecipitated element in a surface ion-exchanged form. The previously mentioned resistance to thermal sintering that these surface species confer on the supporting SnO_2 gel is evident from the specific surface areas quoted in Table 1.

During the CO–NO reaction at 150°C on 450°C-activated SnO_2–CuO gels, some reduction of the catalysts occurs. This is illustrated in Fig. 2 where $SnO_2 \cdot 0.51CuO$ was treated with CO at 150°C in the "microreactor" and the evolved CO_2 monitored chromatographically. Curve A was obtained on the catalyst freshly activated in argon at 450°C for 18 hr and thus assumed to be essentially free from chemisorbed oxygen. Despite fairly extensive tailing, the large proportion of the reduction occurred within the first 2 hr (e.g., ~70% compared with that obtained after 16 hr). Curve B shows the extent of reaction of the catalyst with CO after attainment of steady state at 150°C in a typical CO–NO mixture used in the above studies, followed by extensive flushing with argon to remove chemisorbed species. Negligible quantities of nitrogenous gases were detected during the passage of CO, indicating that chemisorbed NO had been removed. The volume of CO_2 evolved was very low and compared with the concentrations observed in the tail of Curve A, indicating that the degree of reduction of the steady-state catalyst was of the same order as that obtained by its reduction with CO in the absence of NO.

Under similar conditions, activated SnO_2 gel undergoes negligible reduction, which suggests that it is primarily the copper species which are being reduced. Interestingly, the extent of reduction of $SnO_2 \cdot 0.51$ CuO (calculated from the results of Fig. 2 to be equivalent to an oxygen deficiency of 3.0 mg atom of oxygen/g of catalyst after 2-hr reduction in CO) is of the same order as the copper content of the catalyst (2.7 mg atoms/g).

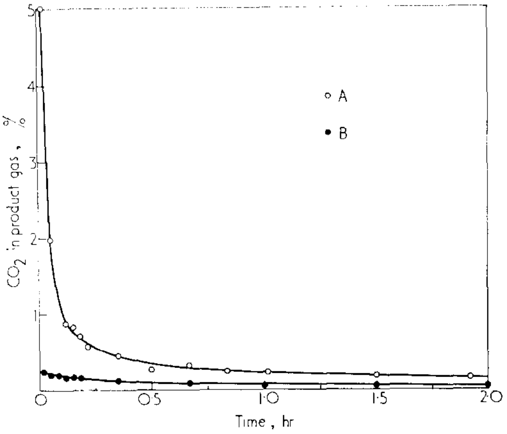

FIG. 2. Reduction of 450°C-activated $SnO_2 \cdot 0.51$ CuO by CO at 150°C. Feed of 10% CO in Ar at 80 cm^3 min^{-1} through 0.5 g of (A) freshly activated and (B) steady-state catalyst.

For those catalysts with Cu : Sn ratios between about 0.2 : 1 and 0.6 : 1, evidence of some reduction of the copper species was afforded by the appearance of a faint but definite coppery lustre on the surface of the shiny black granules after use at 150°C. However, extensive X-ray powder diffraction investigations on these used catalysts showed them to be crystallographically identical with the freshly activated granules, yielding only the SnO_2 phase with no evidence of any crystalline copper species. In addition, full low-temperature (−196°C) nitrogen adsorption isotherms for both freshly activated and used $SnO_2 \cdot 0.55$ CuO were identical, yielding E type isotherms on de Boer's classification, from which the pore-size distributions were calculated using the adsorption branch of the isotherms according to the method of Pierce (*21*). Values for pore volumes of 0.105 cm^3 g^{-1} were obtained with 97 and 85% of the pore volumes containing pores of <50- and <25-Å radius respectively in both cases. These results indicate that (a) negligible pore blocking accompanies reduction of the surface copper species, suggesting that significant segregation of these species from the surface into the pores does not occur and (b), even if this process were to occur, crystallites of sufficient size to permit detection by X-ray diffraction would not result. At present the exact nature of the reduced copper species in these used, active SnO_2–CuO catalysts is unknown, and further investigations, involving ESCA., ESR., and magnetic measurements, are underway in an attempt to clarify this point.

At Cu:Sn ratios above about 0.6:1 both Cu_2O and metallic copper crystalline phases are present in the used catalysts. These are attributable to reduction of the free CuO in these catalysts (*2*), and bulk CuO (prepared by thermal dehydration of $Cu(OH)_2$) was found to undergo similar reduction at 150°C in CO–NO mixtures.

The effect of calcination temperature on the activity and selectivity of a near-optimum composition gel ($SnO_2 \cdot 0.51$ CuO) is shown in Fig. 3, together with the specific surface areas of the used catalyst. For increasing calcination temperatures between 200 and 500°C, only small variations in total NO conversions and N_2 selectivities occur, despite the fact that a significant decrease in specific surface area occurs over this temperature range. This increase in specific activity is presumably attributable to the generation of active sites resulting from more extensive dehydration/dehydroxylation of the surface. Calcination above 500°C, however, results in much more marked sintering, accompanied by a substantial decrease in activity. A similar effect was observed previously for CO oxidation after calcination of $SnO_2 \cdot 0.55$ CuO gel between 450 and 550°C (*2*) and is attributable to segregation of the catalyst into a two-component (SnO_2 + CuO) crystalline system. One notable feature of this sintering effect is that calcination at temperatures above 600°C renders the catalyst almost completely selective for N_2O formation at 150°C.

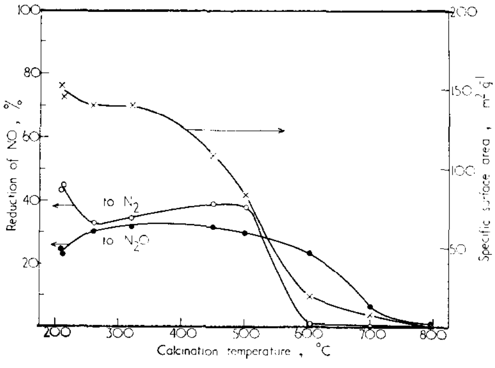

FIG. 3. Effect of calcination temperature on the BET specific surface area and activity for the reduction of NO by CO at 150°C for $SnO_2 \cdot 0.51CuO$. Feed of 14–15% NO in CO at 30 cm^3 min^{-1} through 0.5-g beds.

Mechanistic Studies

Although detailed kinetic studies have not been undertaken in this work, some experiments were carried out using the "microreactor" (which permitted pulsing if required) in order to obtain some mechanistic insight into the CO-NO reaction over SnO_2–CuO gels.

Figure 4 shows the reduction of NO on a near-optimum composition catalyst pre-reduced with CO at 150°C. This treatment has been shown above to produce a degree of catalyst reduction similar to that attained at steady state during the CO–NO reaction at 150°C. In one case the NO was introduced with CO and the reaction monitored at 150°C as a function of time. In the second case the pre-reduced catalyst was flushed with argon for 1 hr at 200°C, after which time neither CO nor CO_2 was detected in the exit gas, and then subjected to 0.5–1-min pulses of NO in argon. The pulses were punctuated by flushing with argon for 10–15 min to permit time for total batch analyses of the individual pulses, and in all cases the mean temperature of the catalyst during the NO pulses was maintained between 150 and 154°C. Negligible quantities of CO_2 were present in the products of the NO pulses, indicating that reaction was with the reduced catalyst and not residual chemisorbed CO, which, in any case, was not present to any significant extent after the argon flush, as shown by subsequent thermal desorption studies.

These results indicate that the predominant mechanism of NO reduction on SnO_2–CuO catalysts is probably one of catalyst redox. The fact that the extent of total NO reduction and the selectivity for nitrogen formation were comparable or even higher during the first NO pulse, compared with the results obtained during the initial introduction of both CO and NO to the reduced catalyst, lend support to a redox mechanism. Subsequent pulses of NO caused a decrease in total NO reduction and N_2 selectivities relative to the results obtained for the CO–NO mixture, obviously attributable to reoxidation of the active, reduced sites, but even so the catalyst continued to show reasonably high activity over several successive NO pulses.

Attempts to obtain comparable data for the reduction of N_2O proved more difficult. The catalyst is very active for the reduction of N_2O by CO, which was found to be complete at temperatures above 120°C under the experimental conditions used, and in fact 120°C represented the self-sustaining temperature under our reaction conditions. For this reason the comparison of N_2O reduction on the pre-reduced catalyst (a) in the presence of CO and (b) in the absence of CO were performed at 120°C, and the results are shown in Fig. 5. Figure 5a shows the effect of adding NO to the self-sustaining CO–N_2O system. After an initial further exothermicity the temperature rapidly dropped to ambient, with a resultant total loss of reaction. In contrast to the highly exothermic reaction accompanying introduction of both N_2O and CO to the pre-reduced catalyst, only very small (<3°C) increases in temperature occurred during introduction of the N_2O pulses to the pre-reduced catalyst at ~120°C, enabling the catalyst temperature to be accurately controlled to 120 ± 1°C during these pulses (Fig. 5b).

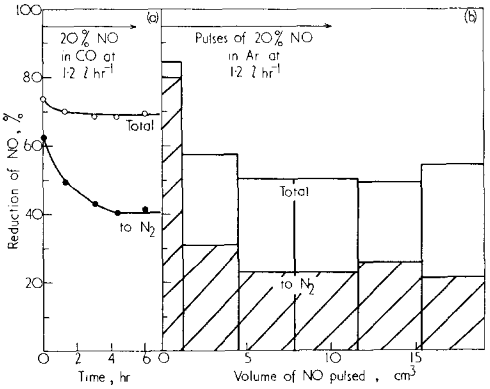

FIG. 4. Reduction of NO at 150°C (a) in the presence of CO and (b) in the absence of CO, on 450°C-activated $SnO_2 \cdot 0.51CuO$ pre-reduced for 16 hr at 150°C with 10% CO in Ar.

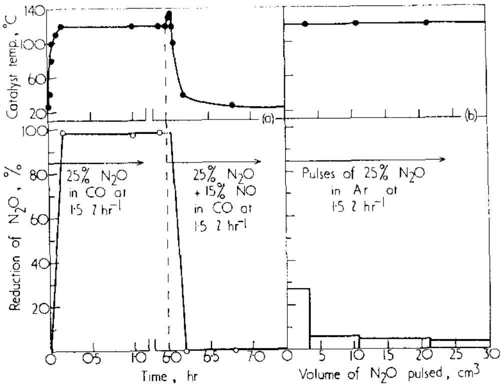

FIG. 5. Reduction of N_2O at 120°C (a) in the presence of CO and (b) in the absence of CO, on 450°C-activated $SnO_2 \cdot 0.51CuO$ pre-reduced for 16 hr at 150°C with 10% CO in Ar.

The results shown in Fig. 5 indicate that the rate of reduction of N_2O by the reduced catalyst is by no means rapid enough to permit explanation of the CO–N_2O reaction rate in terms of catalyst redox, and some mechanism involving reaction of adsorbed CO and N_2O species is thus more likely. These results contrast with those observed for the CO–N_2O reaction at 200°C on SnO_2 alone, where catalyst redox appears to be the predominant mechanism (*20*).

Despite the very high activity of the SnO_2–CuO catalysts for the CO–N_2O reaction, even compared with the CO–NO reaction, significant amounts of N_2O are observed as a product of the latter reaction at 150°C. However, the results of Fig. 5a indicate that NO seriously inhibits the CO–N_2O reaction, presumably by its selective chemisorption on N_2O adsorption sites, thus restricting further reduction of the "intermediate" N_2O produced during the CO–NO reaction.

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