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The Oxidation of CO and C_2H_4 over Metal Oxides

V. SO_2 Effects

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The kinetics of CO and C_2H_4 oxidation over CuO, Fe_2O_3, MnO_2, SnO_2, ZrO_2 and $CuCr_2O_4$ have been studied. The results are compared with those over the other metal oxides reported previously. The reactions are positive fractional order with respect to O_2, CO and C_2H_4 and inhibited by H_2O to various degrees. Co_3O_4, CuO and $CuCr_2O_4$ have higher activity for both CO and C_2H_4 than the other oxides. The reduction in activity as a function of SO_2 concentration in the gaseous phase and the reversibility of the SO_2 effect have been determined. In general, the SO_2 effect on C_2H_4 oxidation is less than that on CO. CuO and $CuCr_2O_4$ are more tolerant to SO_2 than Co_3O_4 and thus could be better candidates for oxidation catalysts for automobile emission control.

INTRODUCTION

The catalytic oxidation of CO and hydrocarbons as a means of automobile exhaust emission control has received wide attention in recent years. Although noble metal catalysts such as Pt and Pd are the best candidates and are more developed at present, a future base metal oxide catalyst, if it can be developed, would be of great importance in view of its natural abundance. For these applications, the kinetic parameters of the reactions at ambient conditions, approaching that prevailing in the exhaust, are needed. It is the purpose of this project to examine the reaction kinetics of CO and hydrocarbon oxidation over various metal oxides, to compare their activity, their tolerance towards possible catalyst poisons such as SO_2 present in the exhaust, their compatability with common catalyst supports and their thermal stability. The results on the noble metal wires, NiO, Cr_2O_3, Co_3O_4 and perovskite-type oxides have been reported (*1–4*). In this report, the results obtained to date on several other metal oxides are presented and compared with those reported previously. Details of the effect of SO_2 on the catalytic activity of the various oxides are included.

EXPERIMENTAL METHODS

The Catalysts

The sources or the preparation of the metal oxide catalysts used are listed in Table 1. Ultrapure or reagent grade chemicals were used as starting materials. The calcined oxides were identified by X-ray diffraction and no second component was detected. The surface areas of the calcined catalysts were determined by Kr adsorption at −195°C and calculated using BET equation. No change of surface area was found after a series of many oxidation experiments.

Determination of the Oxidation Rates

The flow reactor, the mass spectrometric analyses of the inlet and exit gases and the experimental procedures are the same as those reported previously (*1–4*).

TABLE 1
CATALYST CHARACTERIZATION

Catalyst	Source or preparation	Max. calcination temp (°C)	Surface area (m^2/g)
CuO(1)	J.M.[a]	>800	0.52
CuO(2)	Cu (99.999%) + HNO_3	700	0.35
CuO(3)	Alpha Chem. Co.	700	1.45
Fe_2O_3	J.M.	600	3.71
MnO_2	Baker and Adamson Co.	550	0.75
SnO_2[b]	$SnCl_4$ + NH_4OH	1000	1.66
$CuCr_2O_4$(I)	Coprecipitation (5)	700	7.2
$CuCr_2O_4$(II)	Coprecipitation (5)	900	1.84
$CuCr_2O_4$(III)	$Cu(AC)_2$ + $(NH_4)_2Cr_2O_7$	700	2.2
$2CuO{\cdot}Cr_2O_3$	Alpha Chemical Co.	600	5.7
$FeCr_2O_4$	$Fe(NO_3)_3$ + $(NH_4)_2Cr_2O_7$ (6)	1000	2.95
		($CO + CO_2$)	
ZrO_2	$Zr(NO_3)_4$ (J.M.)	1000	11.7

[a] J.M., Johnson-Matthey, specpure grade.
[b] Prepared by K. R. Laud of Ford Motor Co.

RESULTS AND DISCUSSION

The oxidation of CO and C_2H_4 to CO_2 and H_2O over the metal oxides was found to be stoichiometric in almost all cases. Therefore, the rate of oxidation can be measured by the rate of CO_2 produced. The specific rate of oxidation, the rate per unit surface area of the catalyst, and the term of catalytic activity are used interchangeably in this report.

For kinetic studies, the reactions were conducted at near isothermal conditions and low conversions. The partial pressures of the reactants over the catalyst at any time were approximated as the arithmetic mean of the inlet and exit partial pressures. Only the results obtained at $<30\%$ conversion were used for the reaction kinetics evaluations. Because water was found to inhibit the reactions according to a -0.1 to -0.7 order (decreasing inhibition with increasing temperature) water was added to the inlet gas for the hydrocarbon oxidations to minimize the variation of water partial pressure across the catalyst bed. For the CO oxidation, the reaction was carried out either with constant partial pressure of added water or under a H_2O-free condition maintained by passing the inlet gas mixture through a liquid nitrogen cooled trap. To avoid possible reduction of the catalyst surface, the reactants were usually oxygen-rich, i.e., O_2/CO and O_2/C_2H_4 larger than 0.5 and 3, respectively. The ranges of the inlet conditions were O_2, 0.8–4%; CO, 0.5–2%; C_2H_4, 0.1–0.5%; H_2O, 0–1%; SO_2, 0–40 ppm and space velocity 2000–100,000 hr^{-1}. The reaction temperature range was 200–600°C. At <200°C, self inhibition by the reaction products was observed in many cases, and at >600°C appreciable homogeneous oxidation was observed.

In most cases, the log(rate) vs log(partial pressure) plots were linear over a wide range of conditions. Thus, the reaction kinetics could be expressed by the conventional power law as:

$$\text{rate} = k p_{O_2}{}^m p^n_{CO(\text{or HC})} p^l_{H_2O} e^{-\Delta E/RT},$$

where k is the rate constant, p_{O_2}, p_{CO}, p_{HC} and p_{H_2O} are the mean partial pressure of O_2, CO, C_2H_4 and H_2O, respectively. The partial reaction orders, m, n and l are obtained from the slopes of the log–log plots and are usually fractional numbers. ΔE is

the apparent activation energy. Although in most cases, the plots were found to be linear over a wide range of the reaction conditions used in this study, changes of slope did occur in some instances when the range of the partial pressure and temperature increased. For the more active catalysts, the reaction under oxygen-rich conditions became less dependent on the O_2 and more dependent on CO or C_2H_4 ($m \to 0$, $n \geq 1$) with a concomitant sharp decrease in the activation energy above a certain temperature. This is due to the onset of the mass transfer rate-controlling effect, that is, at high temperatures the intrinsic reaction rate became faster than the rate of diffusion of the oxidant through the gas phase to the catalyst surface. The reactions were found to be independent of the concentration of CO_2 in the gas phase at > 150°C. At lower temperatures, the slow desorption of CO_2 (*7*) and strong adsorption of H_2O on the oxide surface could increasingly suppress the reaction with decreasing temperature and result in a higher apparent activation energy. The change in the relative strength of adsorption of O_2 versus CO or C_2O_4 with change in temperature could also cause a corresponding change in the kinetic parameters. Thus, one can obtain a partial reaction order with respect to either reactant varying from a positive order to zero or even to a negative order depending on the ambient conditions used. This may account for some of the discrepancies in reaction orders reported in the literature. For these reasons, the kinetic parameters can only be used within the boundaries from which they have been derived.

The kinetic parameters for CO and C_2H_4 oxidation over the various metal oxides are listed in Tables 2 and 3. Some typical values over the oxides reported previously are also included for the purpose of comparison. Since these results

TABLE 2
KINETIC PARAMETER FOR CO OXIDATION

Catalyst	Temp range (°C)	m	n	$-l$	ΔE (kcal/mole)
Co_3O_4	150–200	0.5	0.5	0.3	20
	300–600	0.1	0.9	0.1	<5
CuO	150–200	0	0.7	>0.3	22
	250–500	0	1.0	0.1	<3
$CuCr_2O_4$	150–250	0	0.7	0	23
	300–500	−0.2	1.2	$-\delta^a$	<3
$LaCoO_3$	150–250	0.3	0.6	δ	19
	300–400	0	0.8	0	3
$BaCoO_3$	300–450	0.3	0.4	δ	12
SnO_2	200–400	0	0.55	—	14
MnO_2	200–500	0.2	0.6	0.15	13
$LaMnO_3$	300–400	0	0.7	δ	12
$La_{0.5}Sr_{0.5}MnO_3$	300–500	0.2	0.8	δ	9
$La_{0.7}Pb_{0.3}MnO_3$	300–450	0	0.75	0	10
Fe_2O_3	200–500	0.3–0	0.9–1.1	0.35	17
$FeCr_2O_4$	300–500	0	0.7	0.1	15
Cr_2O_3	300–500	−0.3–0.4	0.9–0.7	0.2	12–15
NiO	150–500	0.5	0.5	0.3	25 (>220°C) 15 (<220°C)
ZrO_2	400–500	0.2	0.6	δ	17

[a] δ a small fraction, results not quantitative.

TABLE 3
KINETIC PARAMETER FOR C_2H_4 OXIDATION

Catalyst	Temp range (°C)	m	n	$-l$	ΔE (kcal/mole)
Co_3O_4	250–450	0.3	0.5	0.35	23
CuO	300–500	0	1.0	0.15	19
$CuCr_2O_4$	300–500	0.2	0.8	0.15	22
$LaCoO_3$	350–500	0.2	0.8	0	12
$BaCoO_3$	300–500	0.3	0–0.2	δ^a	15
SnO_2	400–500	0.3	0.6	—	—
MnO_2	300–600	0.3	0.65	0.2	20
$LaMnO_3$	400–500	0.5	0.5	δ	17.4
$La_{0.5}Sr_{0.5}MnO_3$	300–500	0.3	0.5	δ	11
Fe_2O_3	300–500	0.15	0.35	0.25	23
Cr_2O_3	250–500	0.4 → 0	0.7	0.25	22
NiO	250–500	0.3	0.5	0.3	25
ZrO_2	400–500	0.2	0.7	δ	13

[a] δ a small fraction, results not quantitative.

were obtained at nearly (but not exactly) differential reaction conditions, variations of $\pm 10\%$ in the parameters are not unexpected. Because the l values are strongly dependent on the reaction temperature, the values given are for the 300–400°C region unless otherwise specified. The water inhibition effect vanished as the reaction entered the diffusion rate-controlling region which is consistent with the supposition that water inhibition was due to adsorption of water on the active sites.

For the purpose of comparison, the specific rates of oxidation of CO and C_2H_4 over the various metal oxides under two particular sets of ambient concentrations are given in Table 4. The reaction rates at other conditions not too far different from those used in this study could be calculated using the kinetic parameters given in Tables 2, 3 and 4. The concentrations of 1% O_2, 1% CO and 0.1% C_2H_4 are chosen as they are near the concentration range in the automobile exhaust. "0% H_2O" instead of "added H_2O" results for CO are listed to avoid the complication of the temperature dependence of the l values.

Some differences in activity and selectivity were found among different preparations of the same metal oxide. Detailed results on various samples of NiO, Cr_2O_3 and the perovskite-type oxides have been reported. In the case of CuO, the catalytic activity for CO and C_2H_4 are highly sensitive to the source material. The highest activity (given in Table 3) was obtained over CuO(2). Only about one tenth of these values were found over CuO(3) and probably can be attributed to the presence of ~0.3% of Na in this sample (*8*).

The activity for CO and C_2H_4 over the $CuCr_2O_4$ catalysts also varied somewhat with the different preparations. The values given in Table 3 for $CuCr_2O_4$(I) were about twice of those for $CuCr_2O_4$(III). $CuCr_2O_4$(II), a mixture of $CuCr_2O_4$ and Cr_2O_3 in undefined proportions, was more active than $CuCr_2O_4$(I) initially, but decayed to a level of about ½ to ⅔ of the latter.

It probably is worthwhile to point out at this juncture that the comparison between the base metal oxides and the noble metal catalysts should not be applied freely due to the large differences in their kinetic parameters (*9*), that is, the oxidation of CO and C_2H_4 over Pt and Pd are negative

TABLE 4
SPECIFIC REACTION RATES

Catalyst	$CO + O_2$[a] Temp (°C)	$CO + O_2$[a] R[c]	$C_2H_4 + O_2$[b] Temp (°C)	$C_2H_4 + O_2$[b] R[c]
Pd(wire)	300	500	300	100
Pt(wire)	300	100	300	12
Au(wire)	300	15	300	0.03
Co_3O_4	200	25 ± 5	300	0.33
CuO(2)	200	11	300	0.6
$CuCr_2O_4$(1)	200	5	300	0.8
$LaCoO_3$	200	2.3	400	0.53
$BaCoO_3$	300	5.3	400	0.1
SnO_2	300	5.2	400	0.4
MnO_2	300	3.4	300	0.04
$LaMnO_3$	300	2	400	0.3
$La_{0.5}Sr_{0.5}MnO_3$	300	1.2	400	0.26
$La_{0.7}Pb_{0.3}MnO_3$	300	0.5	400	<0.05
Fe_2O_3	300	0.4	400	0.06
$FeCr_2O_4$	300	0.33	—	—
Cr_2O_3	300	0.03	300	0.006
NiO	300	0.02	300	0.001
ZrO_2	300	0.013	400	0.002

[a] 1% O_2, 1% CO, 0% H_2O.
[b] 1% O_2, 0.1% C_2H_4, ~0.1% H_2O.
[c] ml CO_2/min-m^2.

order with respect to CO and C_2H_4 and first to second order with respect to O_2 and relatively unaffected by the presence of H_2O. These are quite different from those for the base metal oxides. The ΔE for CO and C_2H_4 over the noble metals is higher than that over the metal oxides. Therefore, the comparison could be quite different if the reaction conditions are far different from those used for Table 4.

In the literature, several attempts have been made to correlate the rate constants for H_2, CO and hydrocarbon oxidation and O_2 exchange reactions over various metal oxides with the metal–O bond strength of the oxides (*10–12*); higher activity is found with lower M–O bond energy. Morooka and his co-workers (*13,14*) have tried to correlate the partial reaction orders m and n (obtained with p_{H_2O} not controlled) observed at 300°C for hydrocarbon oxidation over the metal oxides and noble metals with the M–O bond strength. The general order of activity as shown in Table 4 follows the same pattern. However, the differences in m, n, and ΔE over the various catalysts could scramble the order of activity of the oxides if a different set of reaction conditions was adopted for comparison. The same uncertainty in m and n also exists particularly in the cases where there is a strong temperature dependence for l values. The m and n values obtained at constant p_{H_2O} are different from those obtained at p_{H_2O} not controlled (*1*).

Mutual retardation of CO and C_2H_4 oxidation, when CO and C_2H_4 coexist in the gaseous phase, was found over NiO, Cr_2O_3, $La_{0.7}Pb_{0.3}MnO_3$, Co_3O_4 and noble metals (*1,4,9*). Presumably, it is due to the competitive adsorption of CO and C_2H_4 over the active sites. Over CuO, the slow self-deactivation of CO and the strong inhibition by H_2O at low temperatures masked any effect due to the introduction of C_2H_4. Over $CuCr_2O_4$, the CO oxidation was not retarded by the presence of C_2H_4 when the oxidation of C_2H_4 was negligible. The fact that the reactions are near zero order with respect to O_2 and near first order with respect to CO or C_2H_4 implies much weaker adsorption for CO and C_2H_4 than O_2 on the $CuCr_2O_4$ surface and could be the reason for the absence of strong competition between CO and C_2H_4 for the surface sites. The effect of CO and C_2H_4 oxidation over the Co_3O_4 and $CuCr_2O_4$ catalysts was more difficult to obtain because the temperature required for appreciable C_2H_4 oxidation was usually too high for CO oxidation to be in the intrinsic rate-controlling region.

In a few cases, NiO, Cr_2O_3, Co_3O_4 and $La_{0.7}Pb_{0.3}MnO_3$, about 0.1% of NO was also introduced into the inlet gas to test its effect on the oxidation of CO and C_2H_4. In all cases tested, there was inhibition of

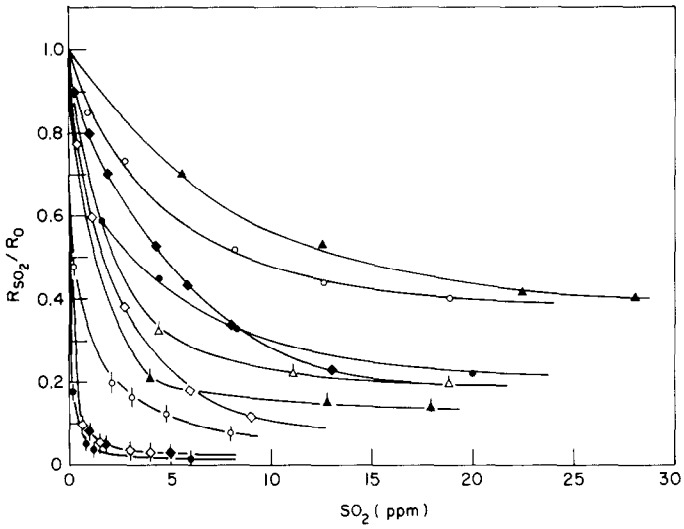

FIG. 1. Reduction in activity vs SO_2 concentration in inlet gas (equil. curve): open points for C_2H_4, filled points for CO; (○, ●) $CuCr_2O_4$, 500°C; (◇, ◆) $CuCr_2O_4$, 400°C; (◇, ◆) Co_3O_4, 600°C; (◇, ◆) Co_3O_4, 500°C; (△, ▲) Cu, 400°C; (△) CuO, 500°C.

the oxidation by the NO, but the effect was completely reversible at the reaction temperatures.

One of the major causes of the catalyst deactivation upon exposure to the exhaust gas has been attributed to the SO_2 poisoning of the catalyst. Therefore, it is of importance to know the tolerance of the catalyst toward SO_2 in the gas phase. For these experiments, SO_2 was incorporated continuously into the reacting mixture in the form of argon containing 0.1% of SO_2. The concentration of SO_2 was varied from 0.5 to several hundred ppm in the inlet gas. Some typical plots for R_{SO_2}/R_0, the rate of oxidation in the presence of SO_2/rate of oxidation prior to the introduction of SO_2 under otherwise the same temperature and inlet conditions, vs the concentration of SO_2 in the gaseous phase, are given in

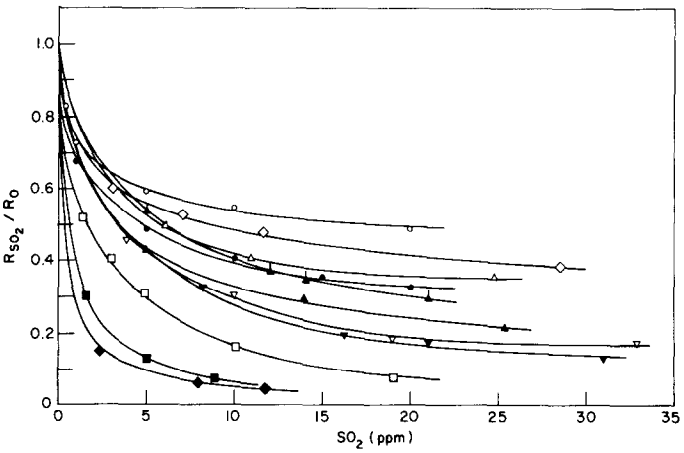

FIG. 2. Reduction in activity vs SO_2 concentration (equil curve): open points for C_2H_4, filled points for CO; (○, ●) SnO_2, 500°C; (△, ▲) Cr_2O_3, 450°C; (▲) Cr_2O_3, 500°C; (▽, ▼) NiO, 500°C; (◇, ◆) Fe_2O_3, 500°C; (□, ■) MnO_2, 600°C.

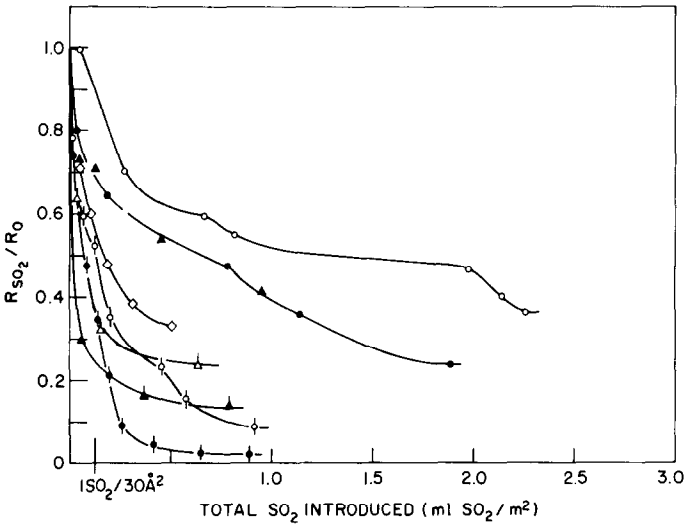

FIG. 3. Reduction in activity vs total amount of SO_2 introduced: open points for C_2H_4, filled points for CO; (○, ●) $CuCr_2O_4$, 500°C; (◇, ◆) $CuCr_2O_4$, 400°C; (△, ▲) CuO, 400°C; (▲) CuO, 500°C; (◇) Fe_2O_3, 500°C.

Figs. 1 and 2. These are equilibrium curves. The R_{SO_2}/R_0 ratios as a function of total amount of SO_2 (summation of concentration × flow rate × time) passed over the catalyst are shown in Figs. 3 and 4. In these plots, the concentration of SO_2 was increased without waiting for equilibrium and the change in concentration was reflected as steps in the plot. When the SO_2 poison is severe, a few ppm of SO_2 in the gas phase can cause near complete poisoning of the catalyst. In such cases, the amount of SO_2 passed over the catalyst to cause total poisoning was found to be less than that required to form a monolayer on the surface if every molecule of SO_2 introduced was taken up by the catalyst. For the catalysts more tolerant to SO_2 a quasi-equilibrium between the degree of poisoning and the concentration of SO_2 in the

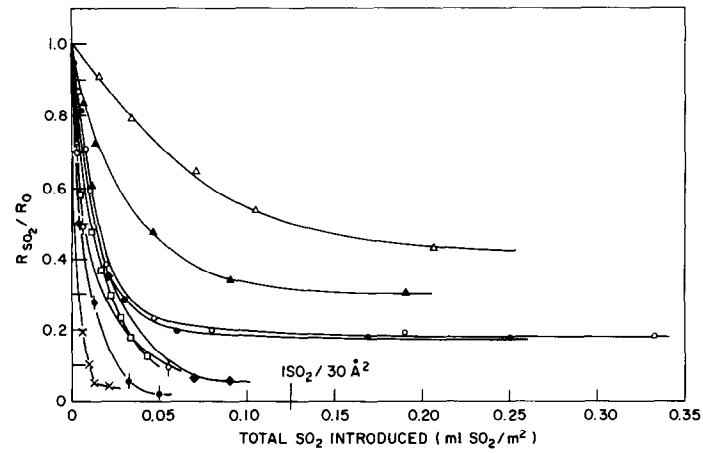

FIG. 4. Reduction in activity vs total amount of SO_2 introduced: open points for C_2H_4, filled points for CO; (▲) Cr_2O_3, 500°C; (○, ●) NiO, 500°C; (◇, ◆) NiO, 400°C; (△) Cr_2O_3, 450°C; (□) MnO_2, 450°C; (◆) Fe_2O_3, 500°C; (×) $CO/FeCr_2O_4$, 500°C.

gas phase could be established. At a constant concentration of SO_2 the rate of oxidation decreases with time to a constant value beyond which further introduction of SO_2 at the same concentration produced no further poisoning until the concentration of SO_2 was changed. Thus, the amount of SO_2 passed over the surface could be much larger than that required to cover the surface. It should be noted that the rates given in Figs. 1–4 are rates based on the same inlet concentration without correction with respect to the change in the partial pressures due to the reaction. Therefore, the actual reduction in activity would be greater than that indicated by the curves.

At the end of the SO_2 poison tests, the source of SO_2 was cut off and the reaction was allowed to continue at the same temperature and inlet conditions. For the catalyst with high SO_2 tolerance, the reaction rate would gradually increase with time. The final constant rate attained, which might take 30 min to overnight, is denoted as R' and the ratio of R' to R_0 (the rate prior to SO_2 introduction under otherwise identical conditions) is shown in Table 5. If the SO_2 poisoning and regeneration experiments were conducted at high temperatures at which the rate was controlled by rate of diffusion, then the ratio of R'/R_0 should be examined at a lower temperature (intrinsic rate controlling region) where the rates are expected to be a function of fraction of surface active sites not covered by SO_2. In the intermediate temperature range, one would see a decreasing R'/R_0 with decreasing temperature. Increasing the regeneration temperature could increase the final R' but only moderately increase the rate of recovery.

It is of interest to note that at constant SO_2 concentration, the degree of poisoning $(1 - R_{SO_2}/R_0)$ increases with decreasing temperature (Fig. 2). Furthermore, Co_3O_4 poisoned at 400°C could not be completely regenerated at 600°C yet the SO_2 poison on Co_3O_4 at 600°C was found to be completely reversible at 600°C. Farrauto and Wedding (*15*) reported that over Co_3O_4 and CuO, the SO_2 poisoning at 400°C was due to chemisorption of SO_2 or SO_3 on the surface while at higher temperatures it was due to sulfate formation. The temperature dependence for the SO_2 poison was also reported by Fishel *et al.* (*16*) Farrauto and Wedding could partially regenerate the activity by washing with water. We noticed that during the regeneration process, the rate of regeneration could be increased by the introduction of 0.2–0.5% of H_2O without altering the final R' value. Presumably water could adsorb on the site vacated by SO_2 to prevent SO_2 readsorption but could not actually cause the desorption of SO_2 from the surface. On a SO_2 poisoned CuO surface, heating at 200–300°C in a stream of He containing 0.5–1% CO for a few minutes could aid the regeneration rate possibly through a reduction reaction to form either COS or S.

In the earlier studies, SO_2 was introduced to the NiO and Cr_2O_3 (*1,2*) surfaces by injection of a few microliters of SO_2 to the inlet gas at a time (high concentration, short time). It was found that the amount of SO_2 injected to affect complete poisoning of the surface was of the order of a monolayer if each SO_2 takes up to 30 Å^2 of the surface. The catalysts poisoned by this method were much more difficult to regenerate than those poisoned at a constant concentration of < 100 ppm. In a separate experiment, SO_2 was passed over $CuCr_2O_4$(1) at 80 and 1000 ppm at 200°C. The weight increase due to the SO_2 uptake was found to be of the order of a monolayer. Over 70% of the SO_2 introduced at 80 ppm could be removed by heating in a nitrogen stream at 500°C while only 20% of that introduced at 1000 ppm was removed under the same conditions. The possibility of sulfate formation at high SO_2 concentration but not at low

TABLE 5
EFFECT OF SO_2

	$CO + O_2$			$C_2H_4 + O_2$		
Catalyst	Temp (°C)	R_{SO_2}/R_0[a]	R'/R_0[b]	Temp (°C)	R_{SO_2}/R_0[a]	R'/R_0[a]
SnO_2	500	0.33	1	500	0.5	1
Fe_2O_3	500	0.04	0.7	500	0.43	1
CuO	300	0.01	<0.05[c]			
	400	0.13	0.5[d]	400	0.2	0.85[e]
	500	0.44	1			
$CuCr_2O_4$	400	0.01	0.7	400	0.04	0.86
	500	0.23	0.8	500	0.4	0.9
Cr_2O_3	450	0.25	0.6	450	0.37	0.8
	500	0.3	0.8			
NiO	500	0.18	0.7	500	0.2	0.8
Co_3O_4	500	0.05	0.33	500	0.05	0.2
	600	0.2	1	600	0.1	0.9
				400	0.02	0.15
$FeCr_2O_4$	500	0.05	0.2			
MnO_2				450	0.13	0.16[f]
	600	<0.1	—[g]	600	0.15	—[g]
ZrO_2	400	0.1	0.1[h]			
$LaCoO_3$	500	0.03	0.15	500	<0.1	0.4
$BaCoO_3$	450	0.25	0.66	450	0.4	0.7
$LaMnO_3$	400	<0.05	~0.1	500	<0.05	~0.1
$La_{0.5}Sr_{0.5}MnO_3$	500	<0.05	~0.1			
$La_{0.7}Pb_{0.3}MnO_3$	400	<0.10	<0.10			

[a] R_{SO}/R_0 = the rate of oxidation in the presence of SO_2/rate of oxidation prior to SO_2 introduction under otherwise same T and inlet conditions.

[b] R'/R_0 = Final constant rate obtained in the absence of SO_2 over SO_2 poisoned surface/rate prior to SO_2 introduction under otherwise same T and inlet conditions.

[c] Treg. = 500°C; $R'/R_0 = 0.7$; CO 1% 250°C 8 min $R'/R_0 = 0.9$.

[d] Treg. = 500°C; $R'/R_0 = 0.9$.

[e] Treg. = 500°C; $R'/R_0 = 1$.

[f] Treg. = 600°C; $R'/R_0 = 0.5$.

[g] Surface prepoisoned by SO_2 at 450°C. Only activity loss due to SO_2 at 600°C can be regenerated at 600°C.

[h] Treg. > 800°C required for complete recovery.

concentration was suggested by Farrauto and Wedding (*15*).

With the exception of Co_3O_4 at 600°C, the reduction in rates for C_2H_4 oxidation by SO_2 was found to be less than that for CO as shown in Figs. 1 and 2. Farrauto and Wedding attributed this difference to the fast poisoning of the carbonyl sites (responsible for CO oxidation) and slow poisoning of the carbonate sites (responsible for hydrocarbon oxidation). The difference we found between the CO and

C_2H_4 was obtained under conditions where the SO_2 was in equilibrium with the surface so that the results do not reflect differences in rates of poisoning of various sites. Fishel and his co-workers (*16*) reported that the SO_2 poisoning on a Cu–Cr–Al oxide catalyst was greater for CO than for hydrocarbons and attributed the oxidation sites for CO and for hydrocarbons to the Cu and Cr sites, respectively. The present results could not determine assignment of active sites. However, in view of the fact that the higher resistance of C_2H_4 oxidation to SO_2 than CO oxidation was found over the various metal oxide catalysts, the reason will have to come from the mechanism of the oxidation of CO and hydrocarbon in general and not from the particular cations involved.

For the purpose of comparison, the tolerance towards SO_2 for the various metal oxides are rated by two parameters: (1) the degree of poisoning R_{SO_2}/R_0, at 500°C with 20 ppm of SO_2 in the gas phase, and (2) the regenerability of the catalyst activity R'/R_0 by continued reaction at 500°C. The results are listed in Table 5. It is shown that the two parameters are parallel. Because of the wide variation in the activity and SO_2 tolerance involved in this evaluation, some extrapolation was unavoidable. Therefore, the results should be treated on a semiquantitative base only.

Based on the results shown above, one can easily arrive at the conclusion that for the best application of the catalytic oxidation method to emission control, the reactor should be operated at high temperature and the fuel should contain low S. Dynamically if a SO_2 tolerant catalyst such as $CuCr_2O_4$ supported on a monolith could pass through the low temperature region (warm-up period) with only a very small SO_2 uptake, then during the normal operation of the car the monolithic catalyst, if mounted near the exhaust manifold, would be at a temperature >600°C at which the effect of SO_2 at the level of 20 ppm in the gas (equivalent to 0.03% S in the fuel) would be relatively small and reversible. However, it will be shown in a separate report that the common catalyst support (wash coat) such as alumina or ZrO_2 can also adsorb SO_2 as tenaciously or more so than the active catalyst itself. Thus the wash coat would serve as a sink as well as a source of S for the catalyst. Once SO_2 is taken up by the supported catalyst, temperatures much higher than 600°C may be required to regenerate the activity. Therefore, it is imperative to minimize the SO_2 exposure by reducing the S content in the fuel as low as possible to maintain the activity of the catalyst.

In conclusion, a good candidate for the oxidation catalyst for the automobile exhaust control should have not only a high intrinsic activity but also good resistance to H_2O inhibition and SO_2 poisoning. Among the metal oxides tested to date, CuO and $CuCr_2O_4$ are by virtue of their higher SO_2 tolerance better choices than Co_3O_4 despite the higher intrinsic activity of the latter. The absence of initial self-deactivation and H_2O inhibition for CO oxidation over $CuCr_2O_4$ and its higher resistance to thermal sintering makes $CuCr_2O_4$ superior to CuO. With proper choice of the catalyst support and ambient conditions modification, higher operating temperature and low S fuel, etc., $CuCr_2O_4$ holds some promise as a substitute for the noble metals for automobile emission control.

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REFERENCES

1. Yu-Yao, Y. F., and Kummer, J. T., *J. Catal.* **28,** 124 (1973).
2. Yu-Yao, Y. F., *J. Catal.* **28,** 139 (1973).
3. Yu-Yao, Y. F., *J. Catal.* **33,** 108 (1974).
4. Yu-Yao, Y. F., *J. Catal.* **36,** 266 (1975).

5. Yureva, T. M., Boreskov, G. K., Zharkov, V. I., Karakchiev, L. G., Popovskii, V. V., and Chigrina, V. A., *Kinet. Catal. (USSR)* **9,** 1063 (1968).
6. Whipple, E., and Wold, A., *J. Inorg. Nucl. Chem.* **24,** 23 (1962).
7. Klissurski, *J. Catal.* **33,** 149 (1974).
8. Kontsonkos, E. P., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Develop.* **4,** 153 (1965).
9. Yu-Yao, Y. F., unpublished results.
10. Popovskii, V. V., *Kinet. Catal.* **13,** 1065 (1972).
11. Krylov, O. V., "Catalysis by Nonmetals," p. 170. Academic Press, New York, 1970.
12. Boreskov, G. K., Popovsky, V. V., and Sazonov, V. A., *Proc. Int. Congr. Catal., 4th, 1968* Pap. 33.
13. Morooka, Y., and Ozaki, A., *J. Catal.* **7,** 23 (1967).
14. Morooka, Y., Morikana, Y., and Ozaki, A., *J. Catal.* **7,** 23 (1967).
15. Farrauto, R. J., and Wedding, B. M., *J. Catal.* **33,** 249 (1974).
16. Fishel, N. A., Lee, R. K., and Wilhelm, F. C., *Environ. Sci. Technol.* **8,** 260 (1974).