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The Oxidation of Hydrocarbons and CO over Metal Oxides

IV. Perovskite-Type Oxides

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Several metal oxides of the perovskite structure have been prepared and used as catalyst for the oxidation of CO and C_2H_4. The oxides include $LaCoO_3$, $BaCoO_3$, $La_xSr_{1-x}MnO_3$ with $x = 0$ to 1, and $La_{0.7}Pb_{0.3}MnO_3$. In general, CO and C_2H_4 are stoichiometrically converted to CO_2 and H_2O. The reaction rates are positive fractional order with respect to both oxygen and the oxidant, and are slightly inhibited by H_2O. The specific reaction rates for the cobaltites are much lower than those over Co_3O_4, but higher than those over the manganites. The reaction over the pure compounds up to 500°C are severely reduced by the presence of a few ppm of SO_2 in the gaseous phase. For $La_{0.7}Pb_{0.3}MnO_3$ prepared in Pt crucibles or doped with 100 ppm of Pt prior to final heating, an increase in activity was observed upon long-time exposure to a reaction mixture containing 10–30 ppm of SO_2. The reaction kinetics over the SO_2-treated Pt-contaminated catalysts are similar to the kinetics over the Pt metal. Details of the SO_2 effect are reported.

INTRODUCTION

Pedersen and Libby (*1*), based on the work of Meadowcroft (*2*) on the electrode oxidation-reduction potential and their own results on the hydrogenation of hydrocarbons over $LaCoO_3$, proposed that rare earth oxides could be used to make inexpensive oxidation catalysts for automobile exhaust treatment. Voorhoeve and his co-workers (*3*) studied the oxidation of CO over PTX[1] and several $La_xPb_{1-x}MnO_3$ and $LaCoO_3$ catalysts using a reacting mixture containing CO and O_2 at a space velocity of ~1000 hr^{-1}. They reported that these perovskite catalysts could rival Pt as an automobile exhaust oxidation catalyst. Parravano (*4*) reported that $La_{0.65}Sr_{0.35}MnO_3$ could catalyze the oxidation of CO at temperatures near its Curie temperature (~373°K). It is well established that the oxidation reactions over various catalysts follow different kinetics depending not only on the nature of the catalyst but also on the ambient conditions and temperature ranges used. This is particularly true in comparison between the noble metal and the base metal oxides. Therefore, experimental data obtained under conditions close to that of the automobile exhaust are needed to determine the catalyst applicability.

As a part of the continuing effort undertaken in this laboratory to evaluate the kinetic parameters of the CO and hydrocarbon oxidation over various catalysts under conditions approaching that in the exhaust gas, a study of the CO and C_2H_4 oxidation over these perovskite-type cobaltites and manganites have been made. The effect on the catalytic activity of H_2O, which constitutes 10% of the exhaust gas, and SO_2, amounting to 20 to 100 ppm in the exhaust gas, have also been studied.

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[1] Trade name of Pt catalyst supported on alumina manufactured by Engelhard Mineral and Chemical Co.

EXPERIMENTAL METHODS

Preparation of the Catalysts

$La_{0.7}Pb_{0.3}MnO_3$ (I) was kindly supplied by Dr. R. J. H. Voorhoeve of Bell Laboratories in the form of HNO_3-etched crystals. This catalyst was grown from a lead borate flux in platinum crucibles (*3*). Spark source mass spectrometric analysis[2] showed ~30 ppm of Pt. X-Ray and atomic absorption analyses also showed the presence of traces of Pt.

$LaMnO_3$ was prepared by grinding $MnCO_3$ and La_2O_3 (2:1 mole ratio) in acetone followed by drying at 200°C and calcination at 1100°C for 20 hr in an alumina crucible.

All the other catalysts were prepared by the coprecipitation method. $Co(NO_3)_2$, $Mn(NO_3)_2$, $La(NO_3)_3$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and $Pb(AC)_2$ in aqueous solutions of the desired proportions were precipitated with NH_4OH. For the manganites, H_2O_2(30% solution) was added simultaneously with the NH_4OH. After the precipitation was completed, the precipitates were filtered and dried at 200°C. For the $La_xSr_{1-x}MnO_3$ preparations, the precipitates were gelatinous; they were dried directly without filtering. To avoid any loss due to partial dissolution, the precipitates were not washed. The dried solids were ground in an agate motor and pestle and calcined at 1100°C for 1-4 days in porcelain or alumina crucibles with the exception of $BaCoO_3$, which was heated at 900°C in a gold crucible.

The X-ray diffraction patterns of the final products showed that they were all of perovskite-type structure, and no second component was detected.

The surface areas of the catalysts were determined by Kr adsorption at -195°C and calculated using the BET equation. The results are shown in Table 1.

TABLE 1
SURFACE AREAS OF THE CATALYSTS

Catalyst	Surface area (m^2/g)
$LaCoO_3$	0.21, 0.45, 1.67
$BaCoO_3$	0.21
$LaMnO_3$	0.27
$La_{0.7}Pb_{0.3}MnO_3$ (I)	0.50
$La_{0.7}Pb_{0.3}MnO_3$ (II)	1.16
$La_{0.7}Pb_{0.3}MnO_3$ (II-W)	2.96
$La_{0.5}Sr_{0.5}MnO_3$	0.93
$La_{0.9}Sr_{0.1}MnO_3$	0.31
$La_{0.7}Pb_{0.3}MnO_3$ (II-Pt)	0.93

$La_{0.7}Pb_{0.3}MnO_3$ (II) was washed with dilute HNO_3 and H_2O and reheated at 1000°C for 1 hr to give $La_{0.7}Pb_{0.3}MnO_3$ (II-W). The acid washing was brownish in color and yielded a brown and white residue, indicating the dissolution of an unknown proportion of the substrate.

The Pt-containing manganites were prepared by wetting the respective manganites with an H_2PtCl_6 solution to give approximately 100 ppm of Pt (by wt). The doped catalysts were reheated at 1000°C for 16 hr.

A Pt/Pb alloy was prepared by wetting Pt black with a $Pb(AC)_2$ solution to give a Pt:Pb mole ratio of 10:1. It was dried, reblended well, and subsequently heated in a porcelain crucible at 1000°C for 20 hr. The dried mass was so small the material so severely sintered that Kr adsorption measurements could not be made.

The Oxidation Rate Measurements

The gases used and the experimental procedures employed for the measurement of oxidation rates have been described elsewhere (*5*). In brief, a flow reactor containing 80 to 250 mg of the unsupported catalyst powders was used. The carrier gas, usually He, containing the desired amount of the reacting gases, was continuously passed through the heated catalyst. The composition of the inlet and the exit gas was determined continuously with an on-line mass spectrometer. The

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[2] MS analysis performed at Battelle Columbus Laboratories.

composition of the inlet gas could be changed at will. Gases, such as H_2O and SO_2, could be added to the gas stream during any stage of the reaction. SO_2 was introduced as a 0.1% SO_2 in argon, and the concentration of SO_2 at the inlet was monitored by the concentration of argon. Prior to each run, the catalysts were heated to 500°C in a stream of He containing 1–2% of O_2 to remove any surface contamination which could evolve from the surface or react with O_2 at temperatures up to 500°C. The temperature was measured by a thermocouple wrapped around the reactor.

RESULTS AND DISCUSSION

The material balance results showed that CO and C_2H_4 were oxidized stoichiometrically to CO_2 and H_2O over all the catalysts included in this report; therefore, the catalytic activity or the rate of oxidation could be measured by the rate of CO_2 produced per unit surface area of the catalyst. Over some of the catalysts studied, but not all of them, the initial rates of oxidation at constant temperature and inlet conditions decreased with time. Such self-deactivation presumably can be attributed to: (a) the accumulation of reaction intermediates, products, or reaction-inhibiting impurities in the gaseous phase such as H_2O on the surface; and (b) change of the catalyst surface area in the presence of the reactants. In this study, the following precautions were taken to minimize this deactivation effect: (i) The CO inlet line was heated to 300°C to remove any Fe carbonyl possibly present; (ii) whenever the H_2O inhibiting effect was found to be severe for CO oxidation, a liquid-nitrogen-cooled trap was inserted at the inlet to remove the water and (iii) the gas mixture was maintained to be oxygen rich in all cases to avoid reduction of the surface. In general, the self-deactivation, if it existed, was less noticeable at temperature higher than 300°C. In this report, only the stabilized rates are included.

The dependency of the specific rates of oxidation on the partial pressures of the reactants was determined at 300, 350, and 400°C for CO oxidation and at 400°C for C_2H_4 oxidation for all catalysts. Wherever the rate and experimental conditions permitted, the kinetic parameters were also studied at other temperatures. Typical results are shown in Figs. 1 and 2. The rates were measured by varying the partial pressure of one of the reactants (the abscissa in the plots) at a time while keeping

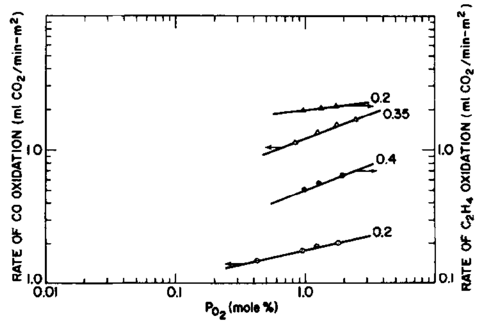

FIG. 1. Rate of oxidation as a function of p_{O_2}, the *m* values are shown. (△) $LaCoO_3$, 250°C, 0.7% CO; (△) $LaCoO_3$, 450°C, 0.3% C_2H_4; (○) $La_{0.7}Pb_{0.3}MnO_3$ (I), 300°C, 1% CO; (●) $La_{0.7}Pb_{0.3}MnO_3$ (I), 300°C, 0.19% C_2H_4.

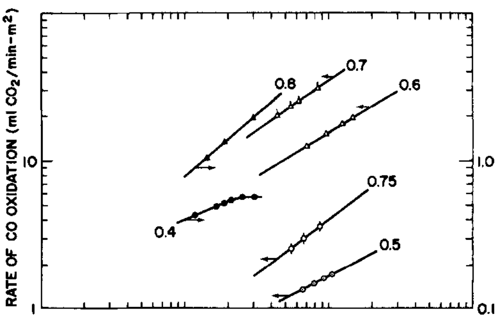

FIG. 2. Rate of oxidation as a function of p_{CO} or $p_{C_2H_4}$, the *n* values are shown
(△) $CO/LaCoO_3$, 300°C, 0.8% O_2
(▲) $C_2H_4/LaCoO_3$, 450°C, 1% O_2
(△) $CO/LaCoO_3$, 250°C, 1.2% O_2
(⊙) $CO/La_{0.7}Pb_{0.3}MnO_3$ (I), 300°C, 0.9% O_2
(⦶) $CO/La_{0.7}Pb_{0.3}MnO_3$ (II), 400°C, 0.9% O_2
(●) $C_2H_4/La_{0.7}Pb_{0.3}MnO_3$ (I), 300°C, 1% O_2.

the partial pressure of the other component (as labeled in the plots) constant to within ±10%. This was achieved by selecting only those points with percentage of conversion <20–30% for the kinetic parameter determinations. The average values of the inlet and the outlet partial pressures of each component were taken as the partial pressures over the catalyst. The linearity in the log–log plots indicates that the reaction rate can be expressed by the following general power law, which has been found to be valid over the other metal oxide catalysts (*5*,*6*) over the range of reactant concentrations used:

$$\text{Rate} = k\, p_{O_2}{}^m\, p_{CO \text{ or } C_2H_4}{}^n\, p_{H_2O}{}^l\, e^{-\Delta E/RT},$$

where rate is expressed as milliliters of CO_2 produced per minute – square meter of catalyst (surface areas given in Table 1); k is the rate constant; m, n, and l are the partial reaction order obtained from the slopes of the log–log plots; and ΔE is the apparent activation energy. The concentration ranges of the inlet gas were 0.8–2.5% O_2, 0.5–1.5% CO, 0.1–0.4% C_2H_4, 0–1% H_2O (if added at the inlet, p_{H_2O} added $> p_{H_2O}$ formed for hydrocarbon oxidation), and 0–50 ppm of SO_2. The space velocities employed were in the range of 30,000 to 100,000 hr^{-1}. The rate dependency on the space velocity, if any, at constant ambient conditions was also checked for each catalyst; and it was found that the rates and the kinetic parameters were generally independent of the space velocity.

The kinetic parameters obtained are summarized in Table 2. In view of the fact that there is appreciable variation in the partial pressure gradient across the catalyst bed (as much as 30%), a variation of ±10% in the m and n values is not unexpected. The dependency of the rates on the partial pressure of water was less accurately determined; furthermore, the water effect was found to decrease with increasing temperature. Therefore, the l values are not given in Table 2. In general, it is of the order of −0.1 to −0.3.

For the purpose of comparison, the spe-

TABLE 2

KINETIC PARAMETERS[a]

Catalyst	Temp range (°C)	$CO + O_2$			ΔE (kcal/mole)	Temp range (°C)	$C_2H_4 + O_2$			ΔE (kcal/mole)
		m	n	l			m	n	l	
$LaCoO_3$[b]	150–250	0.3	0.6	$-\delta$	19	350–500	0.2	0.8	~0	12
	300–400	0	0.8	~0	3					
$BaCoO_3$	300–450	0.3[c]	0.4[c]	$-\delta$[d]	12[c]	300–500	0.3[c]	0 to −0.2[c]	$+\delta$[d]	15[c]
	200–300	0.3[e]	0.1[e]	$-\delta$[d]	14[e]					
$LaMnO_3$	300–400	0	0.7	$-\delta$	12	400–500	0.5	0.5	$-\delta$	17.4
$La_{0.5}Sr_{0.5}MnO_3$	300–500	0.2	0.8	$-\delta$	9	300–500	0.3	0.5	$-\delta$	11
$La_{0.9}Sr_{0.1}MnO_3$	300–500	0.1	0.9	$-\delta$	10	400–500	0.4	0.4	$-\delta$	17
$La_{0.7}Pb_{0.3}MnO_3$ (I)	200–500	0.14	0.6	–[f]	11	200–500	0.4	0.4	–[f]	6.3
$La_{0.7}Pb_{0.3}MnO_3$ (II)	300–450	0	0.75	0	10	300–500	–[g]	–[g]	–[g]	–
$La_{0.7}Pb_{0.3}MnO_3$ (I)[h]	300–500	~1	−0.3 to −0.5	–[i]	20	400–500	>1	0 to −0.5	–[i]	16
$La_{0.7}Pb_{0.3}MnO_3$ (II-Pt)[h]	400	~1	0 to −0.5	–[i]	–	400–500	~1	0 to −0.5	–[i]	13
$La_{0.5}Sr_{0.5}MnO_3$ (Pt)[h]	300–500	1.5	−1	~0	23	–	–	–	–	–

[a] Rate $= k p_{O_2}{}^m p^n_{CO \text{ or } C_2H_4}\, p^l_{H_2O}\, e^{-\Delta E/RT}$, $\delta = 0.1$ to 0.3.

[b] The most active $LaCoO_3$.

[c] Prior to H_2O introduction.

[d] See text.

[e] With H_2O added.

[f] H_2O inhibiting fast, followed by activation.

[g] Activity too low for kinetic studies.

[h] SO_2 treated or in the presence of SO_2.

[i] Strong enhancement by H_2O.

TABLE 3

SPECIFIC REACTION RATES

Catalyst	CO + O_2			$C_2H_4 + O_2$		
	Temp (°C)	% H_2O added	R^a	Temp (°C)	% H_2O added	R^b
$LaCoO_3$[c]	200	0	2.3	400	0	0.52
	300	0	36	500	0	1.67
$BaCoO_3$	300	0	1.7	300	0	0.1[d]
	300	0	5.3[d]	300	0.3	0.7[e]
	300	0.3	10[e]	400	0.3	5.5[e]
$LaMnO_3$	300	0	2	400	0.2	0.3
$La_{0.5}Sr_{0.5}MnO_3$[f]	300	0	1.2	400	0	0.26
$La_{0.9}Sr_{0.1}MnO_3$[f]	300	0	1.3	400	0	0.14
$La_{0.7}Pb_{0.3}MnO_3$ (I)[f]	300	0	1.6	400	0	0.8
$La_{0.7}Pb_{0.3}MnO_3$ (II)	300	0	0.5	400	0	<0.05
$La_{0.7}Pb_{0.3}MnO_3$ (II-W)	300	0	1.5	400	0	<0.05
$La_{0.7}Pb_{0.3}MnO_3$ (II-Pt)	300	0	1.35	400	0	<0.05
$La_{0.5}Sr_{0.5}MnO_3$ (Pt)[f]	300	0	2.0	–	–	–

[a] 1% O_2, 1% CO (ml CO_2/min-m^2).

[b] 1% O_2, 0.1% C_2H_4 (ml CO_2/min-m^2).

[c] The most active $LaCoO_3$.

[d] After CO oxidation at 350°C >20 hr.

[e] After H_2O treatment.

[f] Self-deactivation observed. Stabilized rates quoted.

cific rates at standard sets of conditions are listed in Table 3. With the kinetic parameters given in Table 2, one can calculate the rates under other reaction conditions within the composition and temperature ranges given above. However, extrapolation to conditions far from the given ranges are not warranted.

The Effect of SO_2

Some typical curves are shown in Figs. 3–5 relating the rates of oxidation as a function of the total amount of SO_2 introduced to the catalyst (ml SO_2/m^2 of catalyst). In the case of severe poisoning by SO_2 (Fig. 3), the total amount of SO_2 introduced to cause >90% reduction in rates was approximately equivalent to a monolayer of SO_2. This suggests that SO_2 was so strongly adsorbed on the surface that no relocation of adsorbed SO_2 to some preferred sites was possible. The initial slow decrease in rate of CO oxidation with increasing SO_2 exposure over $LaCoO_3$ could be due to the fact that the reaction was started in the diffusion rate controlling region. For the more SO_2-tolerant catalysts (Fig. 4), an equilibrium between the gas phase and surface SO_2 can be reached; and the reaction rate is a function of SO_2 concentration in the gas phase. In this case, only a small fraction of the SO_2 introduced was taken up by the catalyst. Figure 5 shows some anomalous SO_2 effect observed over $La_{0.7}Pb_{0.3}MnO_3$ (I) and Pt-doped manganite. Details of these cases are discussed below.

The results for the SO_2 effect studies are summarized in Table 4. The ratios of the rate of oxidation in the presence of SO_2 taken after it reached a constant to that before SO_2 introduction for the various catalysts are listed as R_{SO}/R_O in Table 4. It should be noted that the rates R_{SO} and R_O were compared on the basis of the same inlet conditions not corrected for the change of the partial pressures of the reactants due to reaction, and that for the SO_2

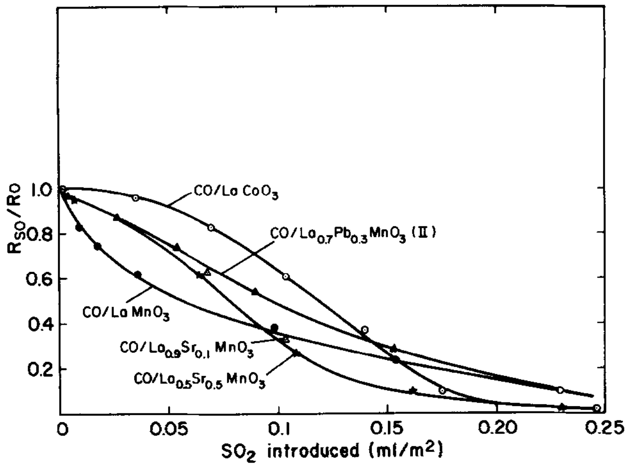

FIG. 3. Rate of oxidation as a function of amount of SO_2 introduced. (○) 500°C, 9 ppm SO_2; (△) 500°C, 5 ppm SO_2; (▲) 500°C, 5 ppm SO_2; (●) 500°C, 10 ppm SO_2; (★) 500°C, 5 ppm SO_2.

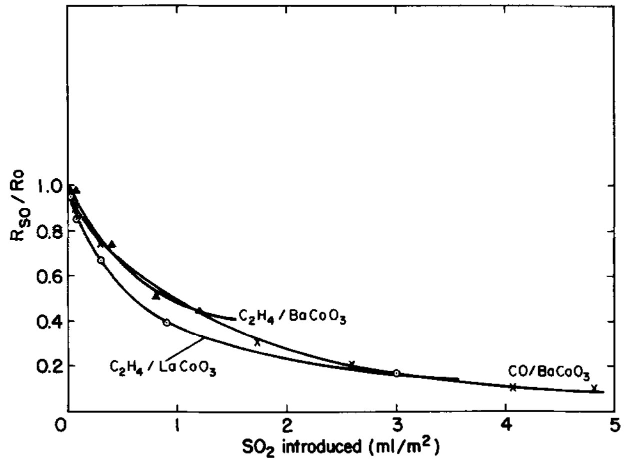

FIG. 4. Rate of oxidation as a function of amount of SO_2 introduced. (▲) 450°C, 5 ppm SO_2; (×) 450°C, 10 ppm SO_2; (○) 500°C, 20 ppm SO_2.

effect studies the reactions were started at relatively high conversions (as high as 70%). Since the reactions were generally positive fractional order with respect to both reactants, the actual SO_2 poisoning would be greater than that indicated by the R_{SO}/R_0 ratios listed.

To study the reversibility of the SO_2 effect, the reactions were continued after the SO_2 source was shut off. The rates in many cases were found to increase slowly with time and eventually reach a constant, R'. This regeneration process could take 30 min to overnight. Sometimes the reaction was carried to higher temperature to see whether higher temperature could enhance the regeneration process. The ratios of the final rate R' to the original rate R_0 prior to SO_2 introduction, under the same temperature and inlet conditions, are listed in the last column of Table 4. The surface area of the catalysts (with the exception of $BaCoO_3$) after the reaction and SO_2 poisoning was not measured because the small amount of the catalysts used. The possibility of the loss of activity due

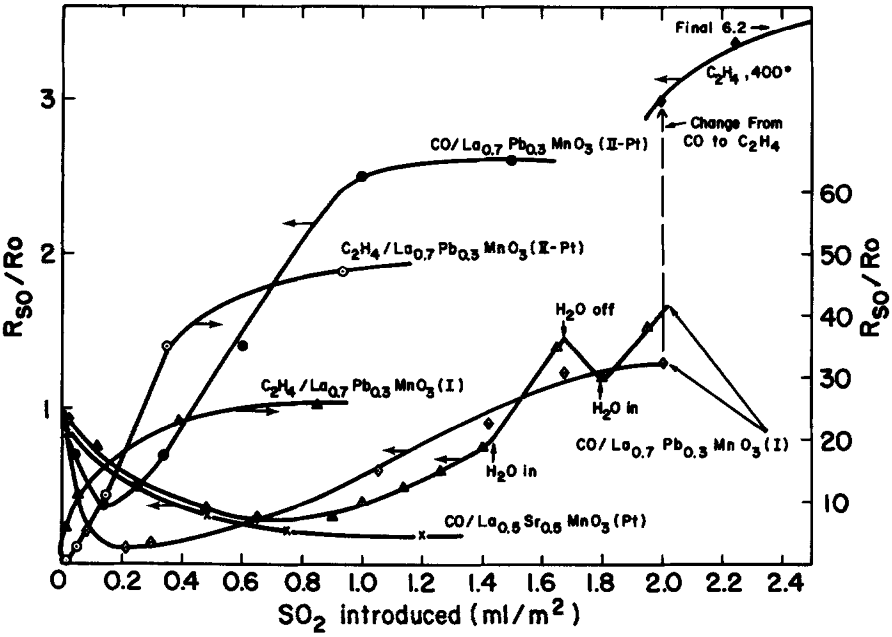

FIG. 5. Rate of oxidation as a function of amount of SO_2 introduced, 20–40 ppm SO_2. (⊙) 500°C; (●) 400°C; (▲) 500°C; (△) 400°C; (◇) 400°C; (×) 500°C.

to decrease in surface area by SO_2 mineralizing the effect is not expected to be significant because: (a) The catalysts were prepared at 1000°C or above and the SO_2 exposure was conducted at relatively low temperature of 400–500°C. (b) The SO_2 poisoning effect in most of the cases was so severe (R_{SO}/R_0 and R'/R_0 less than 0.1) that some decrease in surface area, if it occurred, would not change significantly the overall SO_2 poisoning effect.

$BaCoO_3$. The oxidation of CO over this catalyst under water-free conditions was found to increase slowly with time. After a period of 20 hr at 350°C, an increase in rate of threefold was observed. Kr adsorption on the surfaces before and after the oxidation runs showed no change in the surface area. An even greater and faster increase in activity was observed for CO oxidation in the presence of H_2O. A sevenfold increase in activity for CO and C_2H_4 oxidation was observed after 2 hr of CO oxidation at 300°C in the presence of 0.3% H_2O. Increasing the partial pressure of H_2O caused an immediate decrease in activity followed by a faster increase in activity. The reverse was true for decreasing the partial pressure of H_2O. Removal of H_2O from the inlet gas caused an immediate maximum followed by a slow decay in activity to a value only slightly higher than that prior to H_2O introduction. These observations suggest that there are two modes for the water effect. The fast inhibition by water is probably the same as that observed over the other metal oxides and can be attributed to competitive adsorption of water on the surface active sites. The cause of the slow activation effect is not known. The reversibility of this effect precludes the postulation of surface impurity removal by water. Some surface change under the reaction conditions is possible. $BaCoO_x$ usually exist in the oxygen-deficient state with x varying from 2.4 to 2.8 (*7*). The "$BaCoO_3$" catalyst gave an X-ray diffraction pattern identical with that of $BaCoO_{2.8}$. Under an ambient condition less oxidizing than air, such as

TABLE 4
EFFECT OF SO_2

Catalyst	CO or C_2H_4	H_2O added (%)	Temp (°C)	SO_2 ppm	R_{SO}/R_0	T Regeneration (°C)	$(R'/R_0)_{\mathrm{Temp}}$
$LaCoO_3$	C_2H_4	0	500	4	0.3		
				20	<0.1	500	0.4_{500}
	CO	0	500	10	0.03	500	0.15_{500}
$BaCoO_3$	CO	0.3	450	4	0.17		
		0	450	15	0.25		
		0.3	450	15	0.13	450	0.66_{450}
	C_2H_4	0.3	450	5	0.4	450	0.7_{450}
$LaMnO_3$	CO	0.2	400	10	<0.05	500	$\sim 0.1_{400}$
	C_2H_4	0.2	500	10	<0.05	500	$\sim 0.1_{500}$
$La_{0.5}Sr_{0.5}MnO_3$	CO	0	500	5	<0.05	500	$\sim 0.1_{500}$
$La_{0.9}Sr_{0.1}MnO_3$	CO	0	400	4	0.33		
				30	0.02	500	0.05_{400}
$La_{0.7}Pb_{0.3}MnO_3$ (II)	CO	0	400	50	<0.10	500	0_{500}
						600	$\sim 0.1_{500}$
$La_{0.7}Pb_{0.3}MnO_3$ (I)	CO	0	400	40	0.21 → 1.7	400	0.25_{400} and 1.5_{400}[a]
	↓						
	C_2H_4	0	400	40	6.2	400	6.2_{400}
	C_2H_4	0	500	26	25[b]	500	25_{500}[b]
	↓						
	CO	0	500	26	5	500	5_{500}
	CO	0.6	500	26	5	500	5_{500}
	CO	0	300	40	0.30	300	0.35_{300}
$La_{0.7}Pb_{0.3}MnO_3$ (II-Pt)	CO	0	400	25	3	400	0.9_{400}
	CO	0.8	400	40	3	400	3_{400}
	C_2H_4	0.2	500	20	45[b]	400	45_{500}[c]
$La_{0.7}Sr_{0.5}MnO_3$ (Pt)	CO	0.4	500	10	0.23		
				20	0.13	500	0.22_{500}
							0.26_{400}

[a] R' at 400°C decreased with time after short time SO_2 treatment, remain at high value after long time SO_2 treatment.

[b] Contribution due to change at $p_{C_2H_4}$ at high conversion not corrected, actual value could be smaller.

[c] R' at 300 and 400°C also much higher than R_0, R_0 at 300 and 400°C cannot be measured.

the case used for CO oxidation, a change of the surface to a lower x state is possible. The presence of water could be reducing in nature if the water shift reaction step were involved in the overall reaction. An alternate possibility is that H_2O increases the rate of attack on the surface Ba by CO_2 and frees Co to catalyze the oxidation reactions. The specific activity of this catalyst in the presence of H_2O is comparable to that of Co_3O_4 at low temperature (< 300°C) (*6*) but much less at higher temperatures because the activation energy is higher, and the water inhibition at low temperatures is much more severe over Co_3O_4 than over the $BaCoO_3$ surface. The tolerance toward SO_2 of $BaCoO_3$ is comparable to that over Co_3O_4; therefore, it suffers the same disadvantage as Co_3O_4 in its applicability to automobile exhaust control.

$LaCoO_3$. The specific activity of this catalyst could vary several fold depending on the method of preparation. One of the possible causes is the presence of some highly active Co_3O_4 due to a slight excess of Co in the starting material or incomplete solid state reaction; however, the X-ray diffraction pattern of the more active preparation failed to reveal the presence of any second component. The alternative explanation is that the less active preparations were inadvertently poisoned. In any event,

the specific activity of the most active version was still one order of magnitude less than that of Co_3O_4. Therefore, it would not be the best candidate for the auto exhaust oxidation catalyst. At high temperatures, the kinetic parameters for CO oxidation over the most active $LaCoO_3$ changed because the reaction became controlled by the rate of diffusion of the oxidant molecules (or the product) through the gas phase to (or from) the catalyst surface. The same behavior was also found over the other active catalysts such as Co_3O_4 and $CuCr_2O_4$ (*6*). Its potential in this respect is further limited by the fact that at 500°C a few ppm of SO_2 could irreversibly reduce its activity by 60 to 90%.

The $La_xSr_{1-x}MnO_3$ *catalysts.* The kinetic parameters and the specific activities of $LaMnO_3$, $La_{0.5}Sr_{0.5}MnO_3$, and $La_{0.9}Sr_{0.1}MnO_3$ were quite similar. The rates were of the same order of magnitude as those found over MnO_2. They were about one and two orders of magnitude less than those over the cobaltites and Co_3O_4, respectively. SO_2 in the range of a few ppm in the gas could irreversibly reduce the activity by over the 90%, the same as that found over MnO_2.

The $La_{0.7}Pb_{0.3}MnO_3$ *catalysts.* The kinetics and activity for CO oxidation over the two $La_{0.7}Pb_{0.3}MnO_3$ catalysts were similar to those found over the other manganites, but the activity for C_2H_4 oxidation over (I) was much higher than that over (II). The specific activity over the acid-etched powder (II-W) was higher than that over (II). Voorhove *et al.* (*3*) reported a large increase in CO oxidation activity after acid-etching their $La_{0.7}Pb_{0.3}MnO_3$ crystals, but they did not report the surface area of their samples. Catalyst (II) showed little change in activity with time, while (I) suffered slow self-deactivation with time. It was found that heating the catalyst (I) at 500°C in an enclosed He atmosphere prior to use could minimize the self-deactivation effect.

A striking difference was observed upon introducing SO_2 into the reaction gas at 400°C and above. Over (II), the usual decrease in reaction rate with increasing SO_2 exposure was observed; and finally the catalyst lost irreversibly more than 90% of its activity at 400°C, the same as that observed over the other manganites. Over (I) at 400°C upon admitting SO_2, the activity initially decreased with time to a minimum, followed by a slow increase with time to a value 1.2 to 4 times of its original activity (Fig. 5). H_2O could enhance the rate of the SO_2-induced activation process. Upon removal of SO_2 from the gaseous phase, the activity in the absence of H_2O would decrease with time. Readmitting H_2O or SO_2 or both would again restore the high activity. At 500°C, the increase in activity in the presence of SO_2 was much faster than at 400°C; and the final activity reached 7–8 times the initial value for CO and 50 times for C_2H_4. The new high activity did not change upon removal of SO_2 from gaseous phase. Again H_2O could hasten the activation. At 300°C, the effect of SO_2 was inhibiting; that is, decreasing activity with increasing SO_2 exposure. Upon removing SO_2 from the gas stream, there was a slight recovery in activity; the final rate of oxidation was much less than that prior to SO_2 introduction. Over the SO_2-treated surfaces, both in the presence or absence of SO_2, the kinetic parameter of the reaction changed to: $m \sim 1$, $n = -0.3$ to -0.5, and $\Delta E > 20$ kcal/mole from positive fractions for m and n, and ΔE of 10 kcal/mole over the same catalyst prior to SO_2 exposure. The same SO_2-induced change in kinetics parameters was also observed for C_2H_4 oxidation. Since the SO_2 poisoning of the catalyst surface is one of the most important problems in the application of catalyst to the automotive exhaust control, particularly for the base metal oxide catalysts, this unusual SO_2-induced activation effect merits some further study even though the activity of these manganites (after SO_2

treatment at 500°C) is still far below that of the spinels such as Co_3O_4 and $CuCr_2O_4$.

It was found in this laboratory and also reported by others (*6,8,9*) that the kinetic parameters for CO and C_2H_4 oxidation over noble metal catalysts such as Pt are: $m = 1$ to 1.5, $n = -0.5$ to -1, $\Delta E \sim 30$ kcal/mole, and the reactions are slightly and reversibly inhibited by SO_2. These kinetic parameters are similar to those obtained over the SO_2-treated $La_{0.7}Pb_{0.3}MnO_3$ (I) surface. The specific activity for CO and C_2H_4 oxidation over Pt at 400°C under the ambient conditions as those listed in Table 3 were found to be 3 or 4 orders of magnitude greater than those over the manganites. Therefore, a few square centimeters of Pt per square meter of the manganite present on the surface would be sufficient to give activities comparable to those over the SO_2-treated manganites. Based on these kinetic and rate considerations and the fact that ~ 30 ppm of Pt was detected in the $La_{0.7}Pb_{0.3}MnO_3$ (I) sample, it is speculated that Pt might be the source of the SO_2-induced activity. Since it was difficult to ascertain the amount of Pt on the surface, the indirect study on the Pt-doped manganites was made. A strong SO_2-induced activity was obtained over the Pt-doped $La_{0.7}Pb_{0.3}MnO_3$ (II) with the same kinetic behavior as those observed over $La_{0.7}Pb_{0.3}MnO_3$ (I). But over the Pt-doped $La_{0.5}Sr_{0.5}MnO_3$, SO_2 caused loss of activity at 500°C without the turnaround phenomenon displayed over the $La_{0.7}Pb_{0.3}MnO_3$ (II-Pt). The oxidation reactions over the SO_2-poisoned $La_{0.5}Sr_{0.5}MnO_3$ (Pt) follow the same kinetics as that for Pt. These results suggest that Pt in the $La_{0.7}Pb_{0.3}MnO_3$ catalysts is probably bonded or covered by Pb. The role of SO_2 is then to free the Pt through the formation of $PbSO_4$. H_2O could aid this Pt uncovering process by increasing the diffusion of the $PbSO_4$ from the vicinity of Pt. The rate and extent of this Pt uncovering process increased with temperature. At low temperatures, the SO_2 could inhibit the reaction of adsorption on the manganite as well as the Pt surface. The minimum in the R_{SO}/R_0 vs SO_2 exposure curves (Fig. 5) and the low activity at 300°C after SO_2 exposure indicate that the manganite surface is severely poisoned by SO_2. This (Pt$-$Pb) + SO_2 to Pt + $PbSO_4$ supposition was further substantiated by the results obtained over a Pt–Pb alloy (10:1); in that case, the activity over the alloy was very low, but an increase in activity of about 100-fold was observed upon the admission of SO_2 to the reacting stream.

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