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Specificity of Catalysts for the Oxidation of Carbon Monoxide–Ethylene Mixtures*

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The specificity of five different catalysts for the oxidation of ethylene and carbon monoxide was determined in a microcatalytic reactor at temperatures from 50° to 600°C. On all five catalysts carbon monoxide oxidized more readily than ethylene. Complete removal of carbon monoxide occurred on the cobalt oxide at room temperature, on the copper oxide-chromium oxide on alumina catalyst at 100°C, on both copper oxide and iron oxide at 200°C, and on chromium oxide at 450°C. On cobalt oxide, iron oxide, chromium oxide, and the copper oxide-chromium oxide on aluminum oxide the presence of carbon monoxide enhanced the oxidation of ethylene. Conversely the presence of ethylene inhibits the oxidation of carbon monoxide markedly in the case of cobalt oxide and iron oxide. Significant chemisorption at any temperature was not observed for chromium oxide or copper oxide. The other three catalysts showed significant quantities of chemisorption for both ethylene and carbon monoxide. With chromium oxide, ferric oxide, and cobalt oxide, hydrogen was produced in amounts up to 2% of the hydrogen in the initial ethylene.

INTRODUCTION

Cooperating with the Public Health Service, U. S. Department of Health, Education and Welfare, the Bureau of Mines is investigating catalysts for the oxidation of noxious components in automobile exhausts. Automobile exhaust contains a wide variety of hydrocarbons and oxygenated compounds, each with its own potential for producing eye irritation, lung irritation, plant damage, and smog. The presence of one component in a reaction mixture often affects the reaction rate of another and *vice versa*. The occurrence of such effects will influence the relative distribution of components in the treated exhaust and will determine in part whether oxidation over any particular catalyst will produce an improved exhaust. The present paper is an investigation of such interactions.

The "California Standards for Ambient Air" (*1*) set permissible limits of carbon monoxide and hydrocarbons in exhaust gases. The interaction of carbon monoxide and the hydrocarbon ethylene over catalysts under oxidizing conditions is considered pertinent for evaluation. Five catalysts were chosen for the study. These are copper oxide, cobalt oxide, ferric oxide, chromium oxide, and a copper oxide-chromium oxide supported on alumina. The latter catalyst has been studied extensively in tests with the exhausts from a single cylinder engine (*2, 3*) and in dynamic flow reactor tests (*4*) and will be used in projected road tests. Two of the catalysts, copper oxide and chromia, represent components of the above composite catalyst. The cobalt oxide catalyst was previously shown to be exceptionally active in microcatalytic studies on a series of five carbon

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hydrocarbons (*3*, *5*). The iron oxide was also part of the microcatalytic study (*3*, *5*) and was chosen to represent the behavior of an inexpensive, nonstrategic catalyst of medium activity.

EXPERIMENTAL

Microcatalytic Reactor

The microcatalytic reactor was based on an apparatus first described by Kokes and co-workers (*6*). The system (Fig. 1) is composed of the microcatalytic reactor and a two-stage in-series chromatographic assembly which utilizes oxygen as a carrier gas. The use of oxygen as a carrier has been described previously (*3*, *5*). The carrier gas flows successively through a pressure regulator, a sample injector, and the reactor and then into the two-stage gas chromatographic system capable of detecting and measuring the amounts of ethylene, carbon monoxide, carbon dioxide, and hydrogen present. Samples of ethylene, carbon monoxide, or a $3{:}1{::}\mathrm{CO}{:}\mathrm{C_2H_4}$ mixture are injected into the system through a six-way valve from a manifold of cylinders. The chromatographic unit was calibrated for retention time of each of the reactants and products. A stream of oxygen, 40 cc STP/min, serves both as the carrier gas for the chromatographic column and as a reactant. The fused silica reactor is heated electrically. The temperature is recorded and controlled to ±2°C by a recording-controlling potentiometer. The catalyst, about 5 cc in volume, is held in the center of the reactor by a layer of quartz chips at the top and bottom.

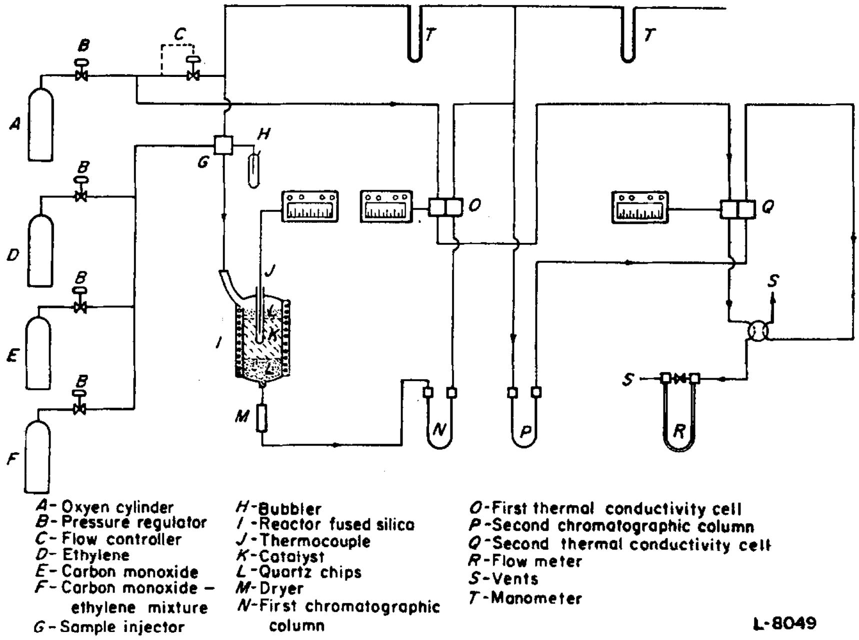

FIG. 1. Flow diagram of microcatalytic reactor for oxidation of carbon monoxide-ethylene mixtures with two-stage chromatographic unit.

The first chromatographic column, 40 ft of $^{5}/_{16}$-inch copper tubing containing 30- to 60-mesh Columpak with 30% by weight hexamethylphosphoramide, and the second chromatographic column, 11 ft of $^{5}/_{16}$-inch copper tubing containing 20- to 30-mesh 13X molecular sieve, are each operated at 28°C. After each column, a Gow-Mac thermal conductivity cell is used to determine differences in thermal conductivity between the reaction stream and a reference stream of oxygen.

For each temperature studied 5 cc (STP) of the test gas is introduced through the sample injector into the carrier gas up-stream of the reactor. As the oxygen carrier stream sweeps the injected gas through the reactor vessel, reaction products are formed and these are swept through the chromatographic system. The first column resolves ethylene and carbon dioxide in the gas mixture (Fig. 2). After passage through the second column the hydrogen and carbon monoxide peaks are resolved as shown (Fig. 2). A carbon balance is made from the areas under each chromatographic peak on the test at each temperature. Failure to achieve a carbon balance indicated that a portion of the charge had remained as a polymerized or chemisorbed material on the catalyst. A blank experiment with quartz chips substituted for the catalyst charge produced no deposit of polymerized or chemisorbed material. Following the test at each temperature the catalyst is cleared of adsorbed material by increasing the temperature to 600°C in the presence of the oxygen carrier stream. This procedure oxidizes the adsorbed materials to carbon dioxide which is measured in column 1 and is an independent measurement of the chemisorption. The performance of the catalyst is determined at 50° intervals from 50° to 600°C or to a temperature at which the reactants are completely oxidized to carbon dioxide.

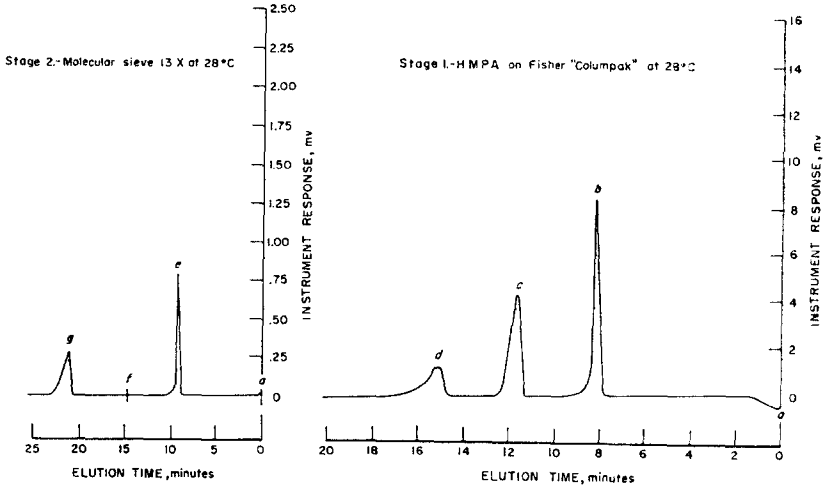

FIG. 2. Typical chromatograms obtained from each chromatographic stage of the microcatalytic unit. Note separation obtained in each column. (a) Disturbances from sample injection. (b) Combined $H_2 + CO$. (c) C_2H_4. (d) CO_2. (e) H_2. (f) Disturbance due to change in polarity. (g) CO.

In oxidation reactions, a substantial amount of oxygen is consumed. The amount of oxygen available for reaction with each injection of the hydrocarbon was measured as follows: By connecting the reactor directly to the thermal conductivity cell the time required for the hydrocarbon wave to pass through the reactor was measured as 45 sec. At the flow rate of 40 cc/min the wave of hydrocarbon and oxygen contains 30 cc or about 13×10^{-4} moles of oxygen. According to the equation, $C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$, 5 cc ($2.2 \times 10^{-4}$ mole) of ethylene requires 6.6×10^{-4} moles of oxygen for complete oxidation. Since nearly twice this amount of oxygen is available in the wave for immediate reaction, an excess of oxygen is present. Carbon monoxide requires less oxygen for complete oxidation than ethylene and therefore presents no problem.

Catalyst Preparation

Chromia, Cr_2O_3, PH-21; cobalt oxide, Co_3O_4, PH-34; copper oxide, CuO, PH-32; ferric oxide, Fe_2O_3, PH-24.1. These catalysts were precipitated from 0.1 *M* aqueous solutions of nitrates with an excess of 0.5 *M* aqueous potassium carbonate solution at about 80°C. The precipitates were filtered and washed until there was no nitrate, as detected by the ferrous sulfate ring test in the wash water, then dried at 100°C, and finally heated in a muffle furnace for 4 hr at 700°C. The cake was crushed and screened to 8- to 12-mesh size.

Impregnated chromia and copper oxide on Alcoa activated alumina H-151, $CuO-Cr_2O_3-Al_2O_3$, PH-235. One-eighth inch spheres of activated alumina were impregnated with a solution of chromic acid and copper nitrate, evaporated to dryness on a steam bath, and fired at 700°C in a muffle furnace for 4 hr. The preparation contained 2% Cu plus 4% Cr on alumina. Closely related catalysts are described in a preceding paper (*5*).

Characterization of Catalysts

Surface areas were measured by the BET method (*7*).

X-ray powder diffraction analyses were made using 0.4-mm diameter extruded

TABLE 1
STRUCTURAL PROPERTIES OF THE SINGLE OXIDE CATALYSTS AFTER USE

Catalyst	Formula	Surface area (m²/g)	Crystal structure	X-ray powder data file[a]
PH-32	CuO	0.5	Tenorite	5-0661
PH-34	Co_3O_4	11.3	Spinel type	1-1152
PH-24.1	Fe_2O_3	13.9	Hematite	6-0502
PH-21	Cr_2O_3	14.0	Hematite type	6-0504
PH-235	$CuO-Cr_2O_3$ on Al_2O_3	350.0	Amorphous	—

[a] X-ray Powder Data File, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa.

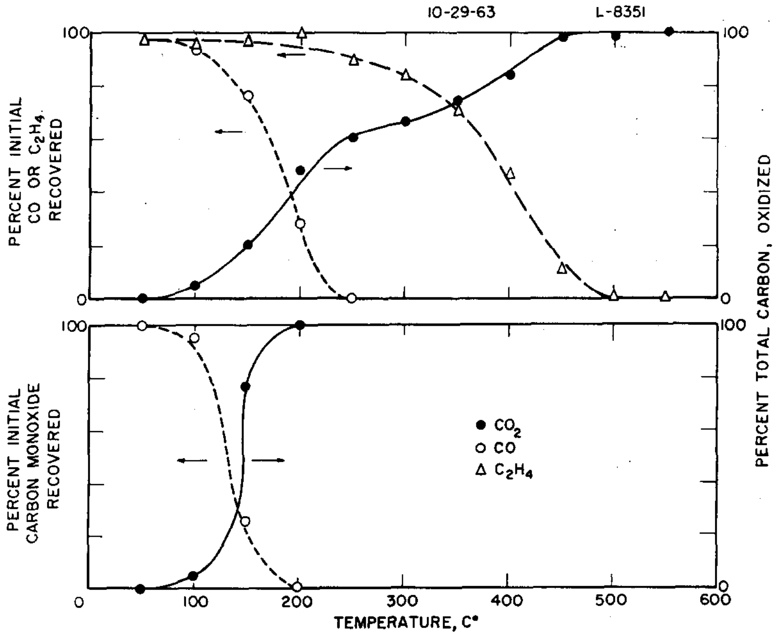

FIG. 3. The oxidation products of carbon monoxide, and a 3:1 mixture of carbon monoxide and ethplene on a copper oxide catalyst.

specimens in 114.6-mm diameter Debye-Scherrer cameras and using iron $K_{\alpha 1, \alpha 2}$ radiation as filtered from the radiation produced by a sealed-off X-ray tube operated at 35 pkv and 10 ma.

Characterizations of the single-component catalysts are given in Table 1. Catalyst PH-235 with a surface area of 350 m^2/g produced a diffraction pattern in which only that of finely divided gamma alumina could be established. Diffraction analyses of the catalyst indicate that no change in crystal structure occurs during use in the microcatalytic reactor.

RESULTS

The data are summarized in Figs. 3 to 7. In these figures the percentage of reactants remaining and the percentage converted to carbon dioxide or chemisorbed are plotted as a function of temperature. In no case does the oxidation of ethylene produce detectable carbon monoxide. Carbon dioxide was plotted as the per cent of the total carbon introduced. In many cases a satisfactory carbon balance could be made from the carbon dioxide formed, the reactant remaining, and the reactant introduced. Where this was not the case the deficiency was considered as chemisorption. In addition, the chemisorption was determined by heating the reactor quickly to 600°C and measuring in the first column the burst of carbon dioxide produced. In all cases the chemisorption as measured by deficiency in the carbon balance and the chemisorption

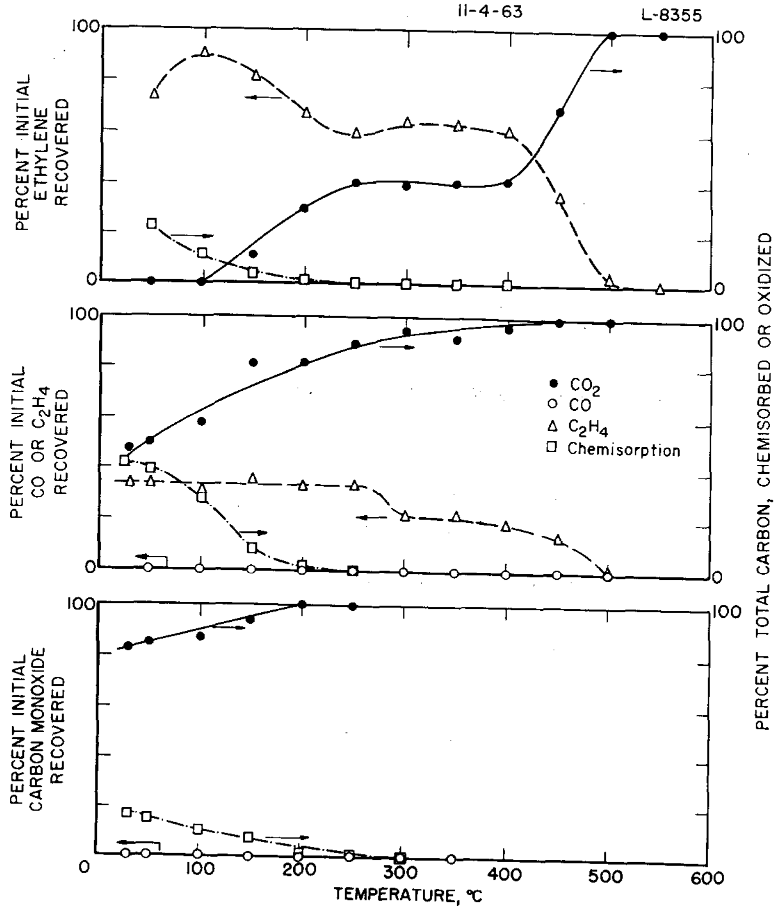

FIG. 4. The oxidation products of ethylene, carbon monoxide, and a 3:1 mixture of carbon monoxide and ethylene on cobalt oxide.

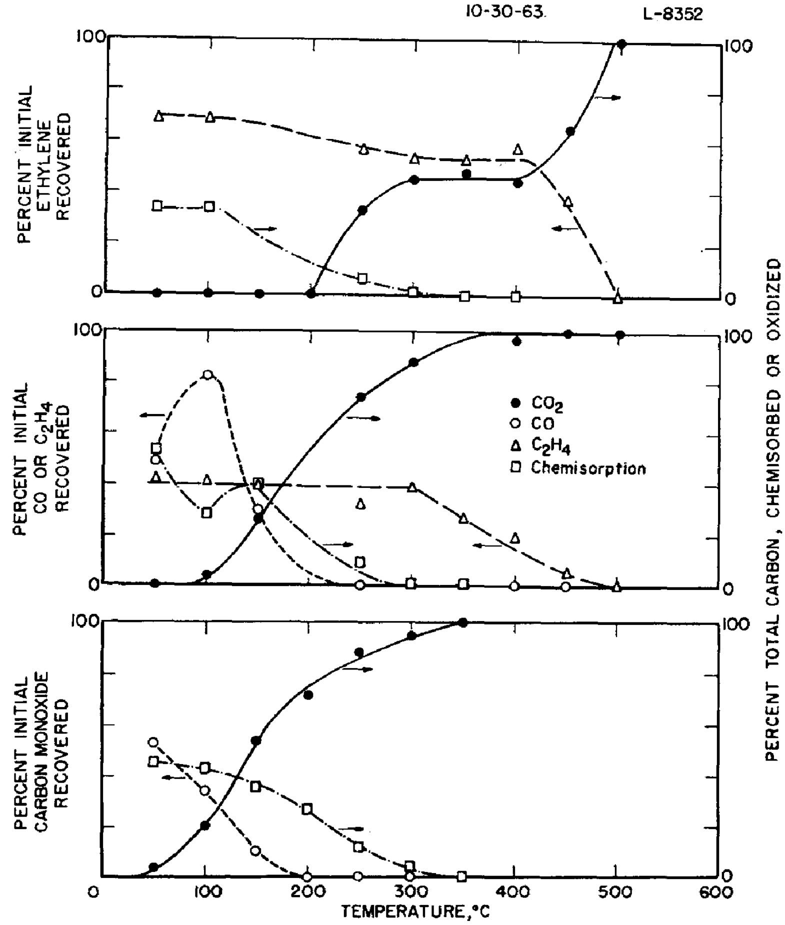

FIG. 5. The oxidation products of ethylene, carbon monoxide, and a 3:1 mixture of carbon monoxide and ethylene on ferric oxide.

as measured by the burst of carbon dioxide obtained on heating the reactor to 600°C agreed within 3 to 5%.

Figure 3 gives the data obtained with copper oxide. Complete oxidation of carbon monoxide occurs at temperatures above 200°C, and no chemisorption was detected at any temperature. The curve for the recovery of carbon monoxide has only a single point of inflection, indicating that oxidation proceeds by a single mechanism over the entire range of conditions. In the oxidation of the mixture of ethylene and carbon monoxide the curves for the recovery of both gases also had only single inflection points. The carbon monoxide seems to be slightly more difficult to oxidize in the presence of ethylene than in its absence.

Figure 4 presents the oxidation of carbon monoxide and ethylene over cobalt oxide. Carbon monoxide is even more readily oxidized over this catalyst than over copper oxide since no recovery of carbon monoxide was possible at any temperature. A small amount of chemisorption of carbon monoxide was evident up to 300°C. The plot for ethylene has at least two points of inflection, which means that the reaction proceeds by two different mechanisms in two different temperature ranges. A slight amount of chemisorption occurred below 200°C. In the reaction of the mixture of

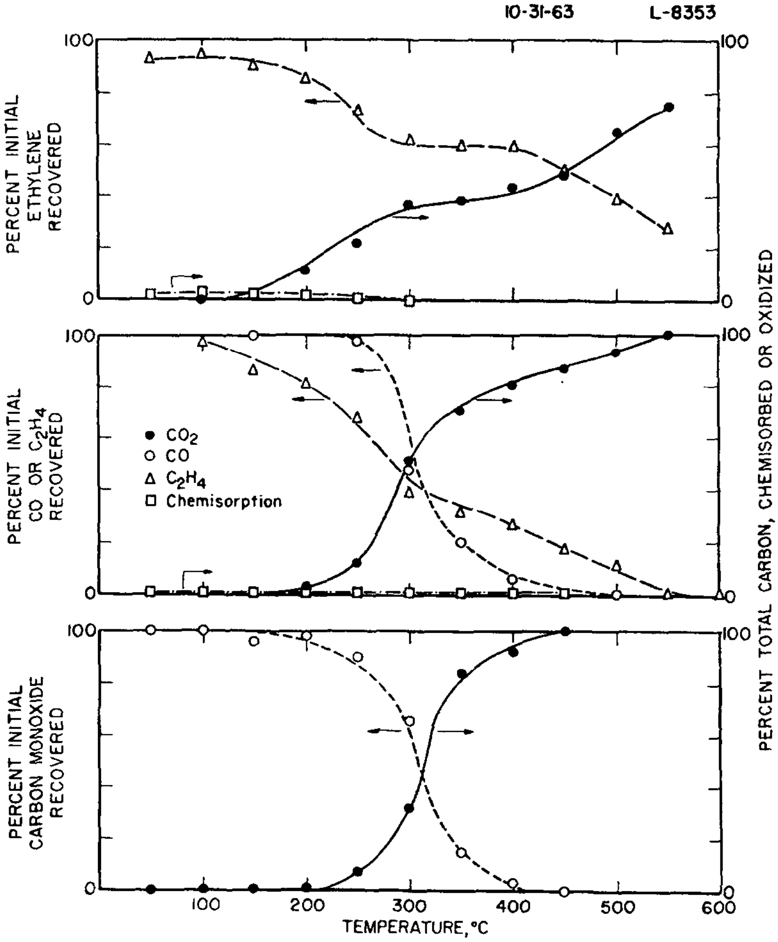

FIG. 6. The oxidation products of ethylene, carbon monoxide, and a 3:1 mixture of carbon monoxide and ethylene on a chromia catalyst.

ethylene and carbon monoxide, carbon monoxide appears to augment the oxidation of ethylene as shown by the larger percentage of ethylene removed from the mixture compared with that removed from pure ethylene at the same temperature. At all temperatures the mixture oxidized more completely over cobalt oxide than over copper oxide. The ethylene recovery curve also shows two points of inflection in the presence of carbon monoxide.

Figure 5 represents the oxidation of ethylene, carbon monoxide, and a mixture of carbon monoxide and ethylene over an iron oxide catalyst. The carbon monoxide oxidation is appreciable even at room temperature and no carbon monoxide remains above 200°C. However, of the three catalysts so far discussed, iron oxide is least effective in oxidizing carbon monoxide. The reaction shows only a single point of inflection. A considerable amount of carbon monoxide was chemisorbed. The oxidation curve for ethylene over iron is complex, suggesting again that oxidation proceeds by two different mechanisms. Ethylene is also strongly chemisorbed on iron oxide. The combined reaction of carbon monoxide and ethylene shows inhibition of the oxidation of carbon monoxide by ethylene and an augmentation of the oxidation rate of ethylene by carbon monoxide. A sizeable

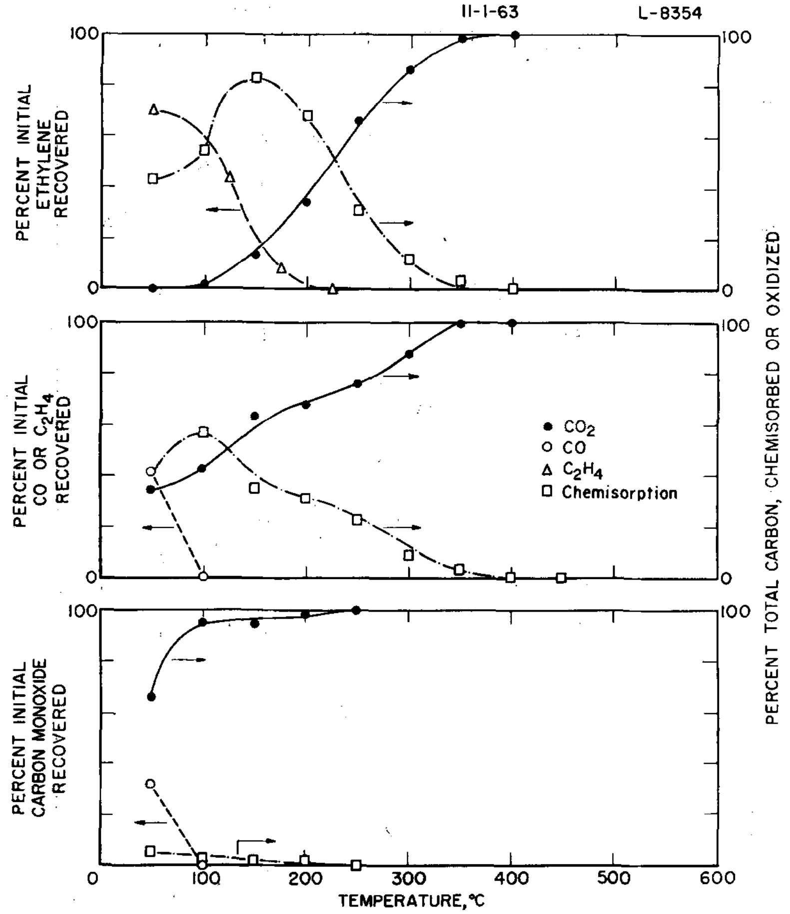

FIG. 7. The oxidation products of ethylene, carbon monoxide, and a 3:1 mixture of carbon monoxide and ethylene on copper oxide chromia impregnated on alumina.

fraction of the reactants remains chemisorbed at temperatures below 300°C. The minimum and maximum in the chemisorption curves suggest activated adsorption.

Figure 6 shows the oxidation of carbon monoxide, ethylene, and a mixture of carbon monoxide and ethylene over a chromia catalyst. The recovery curve for carbon monoxide has a single inflection point. Of the four single oxide catalysts tested, chromia required the highest temperatures; that is, chromia was the poorest of the single oxides for the oxidation of carbon monoxide. On the other hand, chromia chemisorbs no carbon monoxide. The curve for the recovery of ethylene is complicated by at least two points of inflection showing two different mechanisms at different temperatures.

Figure 7 shows the oxidation of carbon monoxide and ethylene over a composite copper oxide-chromium oxide on alumina catalyst. This catalyst proved the most active of those tested for the oxidation of carbon monoxide. The chemisorption of carbon monoxide is negligible. Complete oxidation of ethylene is possible at a lower temperature (350°C) than on other catalysts. The maximum in the chemisorption curve for ethylene suggests an activated adsorption process. Oxidation of ethylene occurs at lower temperatures and is complete at temperatures lower than those observed in the oxidation of the mixture. The

TABLE 2

EFFECT OF CARBON MONOXIDE ON THE OXIDATION OF ETHYLENE AND VICE VERSA

Catalyst	Temperatures required for 75% removal of reactant					
	Ethylene (°C)	Carbon monoxide (°C)	Ethylene with carbon monoxide		Carbon monoxide with ethylene	
			(°C)	(Δ°C)[a]	(°C)	(Δ°C)[a]
CuO	—	150	400	—	205	+55
Co_3O_4	470	<25	285	−185	<25	—
Fe_2O_3	470	120	355	−115	155	+35
Cr_2O_3	560	330	410	−150	335	+5
CuO-Cr_2O_3-Al_2O_3	145	60	<50	<−95	65	+5

[a] Difference between the temperature required for the pure compound and that required for the same compound in the mixture.

presence of carbon monoxide increases the oxidation of ethylene but the presence of ethylene does not in turn increase the oxidation of carbon monoxide. Carbon monoxide was oxidized completely at 100°C, both alone and in the presence of ethylene.

Molecular hydrogen in amounts up to 3% of the combined hydrogen in the reactant hydrocarbon was evolved over chromia between 300° and 500°C in the microcatalytic reactor. Smaller amounts were produced over iron oxides and only traces over cobalt oxide. No hydrogen was detectable in the reaction products formed over copper oxide and copper-chromia-alumina catalyst. The tendency of the catalyst to form hydrogen may be related to the capacity to dehydrogenate hydrocarbons. The relative order of dehydrogenation activity of the present catalysts is Cr > Fe > Cu, the same order as the tendency to produce hydrogen. The ability of the catalyst to dehydrogenate must be accompanied by an inability of the catalyst to oxidize hydrogen at a rate sufficient to prevent its escape from the reactor.

DISCUSSION OF RESULTS

Table 2 presents the temperatures required for removal of 75% of the initial reactants. The temperatures indicated are an inverse measure of catalytic activity (*5*) and they permit the comparison of activity with and without the presence of another reactant. Thus, the activity of iron oxide in the oxidation of ethylene can be considered by itself (column 2) and in the presence of carbon monoxide (column 4). Similarly the activity of iron oxide in the oxidation of carbon monoxide can be considered by itself (column 3) and in the presence of ethylene (column 5).

In all the cases considered here, the effect of the presence of one constituent of the mixture of ethylene and carbon monoxide was to bring the rates of oxidation of both components closer together. The ethylene, the more difficult component to oxidize, was made easier to oxidize by the presence of carbon monoxide. Conversely carbon monoxide, the easier component to oxidize, was made more difficult to oxidize by the presence of ethylene.

From the data in Table 2 the sequence of catalytic activity of the five catalysts can be determined as shown in Table 3. The comparison of the activity sequence for pure ethylene with that for pure carbon monoxide shows that cobalt oxide is much better for the oxidation of carbon monoxide than for ethylene. The other catalysts remain in nearly the same relative positions in both sequences.

The sequence of activity of the oxidation of ethylene in the presence of carbon monoxide is nearly the same as that obtained without carbon monoxide. In every case carbon monoxide made the ethylene easier to oxidize by 95°C or more. The activity improvement was largest with cobalt oxide.

In every case carbon monoxide is oxidized more readily than ethylene but the

TABLE 3

ORDER OF ACTIVITY OF CATALYSTS[a]

	Individual gases as reactants				
Carbon monoxide	Co_3O_4 >	$CuO-Cr_2O_3-Al_2O_3$ >	Fe_2O_3 >	CuO >	Cr_2O_3
	<25°	60°	120°	150°	330°
Ethylene	$CuO-Cr_2O_3-Al_2O_3$ >	Fe_2O_3; Co_3O_4 >	Cr_2O_3		
	145°	470°	560°		
	Mixture $CO + C_2H_4$ as reactant				
Carbon monoxide (with ethylene)	$CuO-Cr_2O_3-Al_2O_3$ >	Co_3O_4 >	Fe_2O_3 >	CuO >	Cr_2O_3
	<50°	285°	355°	400°	410°
Ethylene (with carbon monoxide)	Co_3O_4 >	$CuO-Cr_2O_3-Al_2O_3$ >	Fe_2O_3 >	CuO >	Cr_2O_3
	<25°	65°	155°	205°	335°

[a] Temperatures, °C, are for 75% removal of reactants.

difference in oxidation temperatures is >445°C over Co_3O_4 and only 85°C over $CuO-Cr_2O_3-Al_2O_3$. This range in relative oxidizability over different catalysts is indicative of the importance of specificity and demonstrates the importance of tailoring the catalyst to the exhaust composition in order to achieve the best results.

The order of activity for the oxidation of carbon monoxide in the presence of ethylene is the same as that for the oxidation of ethylene in the presence of carbon monoxide except that $CuO-Cr_2O_3-Al_2O_3$ and Co_3O_4 have changed places (Table 3). In contrast to the oxidation of ethylene in the presence of carbon monoxide, the presence of ethylene inhibits the oxidation of carbon monoxide over two catalysts, Fe_2O_3 and CuO, and has no significant effect in two others, Cr_2O_3 and $CuO-Cr_2O_3-Al_2O_3$ (Table 2).

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