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# A Study of High Temperature Treated Supported Metal Oxide Catalysts

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The oxidation of CO and $C_2H_4$ at 200–400°C over two groups of supported metal oxide catalysts has been studied. The catalysts in group A were mechanical mixtures of presintered metal oxides (CuO, $Co_3O_4$, NiO, and $CuCr_2O_4$, 0.1–10% by wt) with presintered catalyst supports ($\alpha$-$Al_2O_3$, $\gamma$-$Al_2O_3$, and $ZrO_2$) and those in group B were prepared by the conventional method of impregnation of the presintered supports followed by 500°C calcination. With the exception of $Cr_2O_3$, the catalytic activity of group A supported on $\alpha$-$Al_2O_3$ or $ZrO_2$ increased 10–200-fold after being heated at 700°C and above for 10–30 min and reached a maximum at ~900°C, while the catalytic activity of group B remained constant or decreased slightly with increasing heat treatment temperature. The maximum activity per total surface area of group A approached that of the corresponding pair of group B, and was dependent on the composition of the catalyst. The activity of the supported catalyst per total surface area was found to be in all cases less than the corresponding specific activity of the unsupported metal oxide. This phenomenon is discussed in terms of increased dispersion induced by the high temperature treatment. When $\gamma$-$Al_2O_3$ was used as the support the thermally induced activity was much less and usually short-lived, presumably because the rate of chemical interaction and sintering overtook the rate of thermal dispersion.

## INTRODUCTION

It is well documented that the activity of a catalyst can be drastically altered by the support used and its method of preparation. Such effects are strongly dependent on the temperature and the ambient conditions. For automotive exhaust purification, catalysts are required to maintain their activity after long time exposure to the exhaust atmosphere at temperatures of 600–1000°C. Therefore, it is important to examine the support effect under these conditions. Most of the previous work in this field was performed on two types of catalysts: (a) catalysts prepared by impregnation or coprecipitation followed by heating to temperatures which seldom were as high as those which might be encountered in automotive exhaust and (b) dilute solid solutions, e.g., NiO–MgO prepared at high enough temperatures to give an equilibrium composition. The first type of catalyst was initially in a highly dispersed and unstable state and high temperature treatment would bring on physical changes such as sintering, phase transition or pore structure alteration of each component as well as chemical interaction or dissolution. These various processes may have compensating effects on the catalytic activity so that it is very difficult, if not impossible, to resolve the specific contributing factors from the net change in activity. Valuable information on the catalytic process has been obtained from studies of the second type of catalysts (*1*), but often on reactions irrelevant to automotive exhaust purification.

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A mixture of the presintered active component and the support could be useful to study the interaction between the active compound and the support, since physical changes of the individual components are expected to be relatively small. Such mixtures also are used in practical catalysts, particularly for catalysts in which the active component contains two or more different metal ions at fixed stoichiometry and a well-defined structure. For these catalysts, the active compound would have to be prepared, sometimes at very high temperatures, prior to addition to the support which generally is considered as a diluent and/or binding agent.

In a previous communication (*2*), one of us has reported that the catalytic activity for CO, $C_2H_4$, and $C_2H_6$ oxidation of a mixture of $Co_3O_4$ (400°C presintered) and $\gamma$-$Al_2O_3$ (500°C preheated) was much greater than that of a catalyst prepared by impregnation. The activity of the mixture increased after moderate heating (600–700°C), but decreased sharply after calcination at 850°C or above. A mixture of the same $Co_3O_4$ and $\gamma$-$Al_2O_3$, both preheated at 850°C before mixing, on the other hand became more active after 850°C heating. Furthermore, the activities of the mixtures were found to be strongly dependent on the nature of the support used. It was postulated that, at high temperature, either $Co^{3+}$ or $Co_3O_4$ was spreading over the support surface to increase the active surface area. Hüttig (*3*) first reported such an increase in activity for CO oxidation and $N_2O$ decomposition over a ZnO + $Fe_2O_3$ mixture upon heating to 400°C and above. He attributed this to the coating of the surface of one component by the other followed by the formation of a surface molecular film, an initial step of a reaction between mixed solids. Since then, relatively little work has been reported on such effects.

In this investigation, mixtures of several metal oxides with $ZrO_2$, $\alpha$-$Al_2O_3$, and $\gamma$-$Al_2O_3$ have been used for CO and $C_2H_4$ oxidation. The mixtures were treated at 700–970°C either in air or in a stream of helium containing 1–2% $O_2$ and 1–2% CO passing through the sample. In the latter case, complete oxidation of CO took place during these treatments. The activities of these high temperature treated mixtures are compared with their corresponding active metal oxide–support couple prepared by impregnation. The enhancement in activity due to heating is examined on the basis that the active component spreads over the support surface as proposed above.

## EXPERIMENTAL METHODS

Each of the supported catalysts consists of an active metal oxide (amo) and one of the three inert oxides (support). Type MX catalysts were prepared by mixing weighed amounts of the two presintered components, and grinding lightly in an agate mortar until a uniform appearance was obtained. Surface area determinations showed that no measurable increase resulted from the grinding operation. The sources and the surface areas of the starting materials are listed in Table 1. The apparent particle sizes of the powders were examined by optical and scanning electron microscopy. They are: 0.5–10 $\mu$m for the active metal oxides, 2–30 $\mu$m porous lumps for $ZrO_2$, 3–10 $\mu$m, for $\alpha$-$Al_2O_3$. $\gamma$-$Al_2O_3$ was in the form of crushed dried gel with lumpy and large cage structure, the portion that passed the 100 mesh sieve was used for this study. The distribution of the active metal oxide particles in the mixed powders appeared to be quite uniform. Heat treatment at 900°C for 2 hr caused no apparent particle size increase or phase separation. Type IMP catalysts were prepared by the conventional method of impregnating the presintered support with a just sufficient amount of a salt solution of known concentration. They were dried under a heat

TABLE 1

Surface Area of the Starting Materials

| Metal oxides | Source | $T$ calcination (°C) | Surface area ($m^2/g$) |
|---|---|---|---|
| CuO | 99.999% pure Cu + $HNO_3$ | 900 | 0.35 |
| $Co_3O_4$ | Johnson Matthey Co. Specpure | 900 | 0.54 |
| NiO | Johnson Matthey Co. Specpure | 900 | 0.30 |
| $Cr_2O_3$ | Johnson Matthey Co. Specpure | 900 | 1.15 |
| $CuCr_2O_4$(II)[a] | Coprecipitation | 700 | 7.2 |
| $CuCr_2O_4$(I)[b] | Coprecipitation | 900 | 1.56 |
| $\alpha$-$Al_2O_3$ | Linde A | 1000 | 10.1 |
| $\gamma$-$Al_2O_3$ | Dispal[c] | 850 | 93.0 |
| $ZrO_2$[d] | National Lead Co. | 700 | 28.0 |
| | | 1000 | 10.2 |
| $ZrO_2$(JM) | $Zr(NO_3)_4$ of Johnson Matthey Co. | 1000 | 1.0 |

[a] See Ref. (7) XRD identified as $CuCr_2O_4$.

[b] See Ref. (7) XRD identified as $CuCr_2O_4$ (major), $Cu_2Cr_2O_4$ and $Cr_2O_3$ as minor components.

[c] Colloidal $\gamma$-$Al_2O_3$ from Conoco.

[d] In this report $ZrO_2$ refers the calcined product of National Lead Co. colloidal zirconia.

lamp, decomposed in an 250°C oven and calcined at 500°C for 16 hr. The resulting catalysts usually had a uniform color.

The rates of CO and $C_2H_4$ oxidation over these catalyst powders were determined using a quartz flow reactor and an on-line mass spectrometer. The BET surface areas were determined by Kr or $N_2$ adsorption. Details of these techniques have been reported previously (*4*). The reactor was in the form of 7 mm o.d. quartz U-tube with the inlet leg serving as the gas preheater. Thermocouples were secured tightly to the outside of the tube at the sample point and the temperature was recorded simultaneously with the mass spectrometric output by a two-pen recorder. Precaution was taken to insure that data taken for activity evaluation was relatively free of thermal effect. A four-way valve was used to allow point-by-point determination of the inlet and exit gaseous composition. Only points of less than 30% conversion, with majority less than 20% conversion, were used for the activity evaluation. The partial pressures of $O_2$ and CO could be changed at will and their concentrations were generally less than the 2% level. Helium was used as carrier gas and the total pressure was 1 atm. The average values of the inlet and exit partial pressures of each component were used as the partial pressures for kinetic evaluation. The rates (or activity) are expressed as volume of $CO_2$ at STP produced per minute per unit surface area.

Prior to the first oxidation rate determination on a fresh catalyst, the sample as heated at 500°C for 0.5 to 1 hr in a stream of helium containing 1–2% of $O_2$ to remove any $H_2O$, $SO_2$ or organic contaminants acquired on the surface during preparation or storage. The reactions were carried out in oxygen-rich atmosphere in all cases, i.e., the $O_2$/CO ratio at the inlet was always $>0.5$ with CO in the range of 1–2%, and the space velocities range were 50,000–250,000 hr$^{-1}$ (STP). The standard procedure adopted was to determine the rate of oxidation at 200°C and at increasing temperature steps of 50 or 100°C until a temperature where 100% conversion occurred was reached. The sample then was placed in a high temperature furnace so that the two solids could interact for 20–30 min. This high temperature at which the solids were allowed to interact will be designated as the pretreatment temperature throughout this report. The furnace then was removed and the sample was quenched to below the testing temperature, usually to 200–300°C depending on the activity of the catalyst. A furnace preheated to the testing temperature was put around the sample and a series of oxidation rate determinations at increasing temperature steps were made. The temperature of the sample then was raised to a value equal to or higher than the previous pretreatment temperature and the procedure of interaction at high temperature, quenching and rate determination was repeated. For the experiments designated as "heated in air," the samples were heated in a muffle furnace and quenched directly to room temperature in air.

At above 1000°C, most of the oxides studied undergo either phase transition or loss of oxygen to form lower oxides such CoO, $Cu_2O$, and $Cu_2Cr_2O_4$. In addition, $ZrO_2$ transforms from monoclinic to tetragonal and $\gamma$-$Al_2O_3$ to $\alpha$-$Al_2O_3$ (*5–6*). Therefore, the pretreatment temperature was limited to below 970°C.

## RESULTS

### *Unsupported Metal Oxides*

TABLE 2

Specific Rate of CO Oxidation over Unsupported Metal Oxides

| Catalyst | Reaction temp (°C) | Rate[a] ($CO_2$ ml/min-m$^2$); pretreated[b] at (°C): | | |
|---|---|---|---|---|
| | | 500 | 700 | 900 |
| CuO | 250 | 45 | 47 | 50 |
| NiO | 300 | 1.8 | — | 1.5 |
| $Cr_2O_3$ | 300 | 0.03 | 0.07 | 0.08 |
| $Co_3O_4$ | 200 | 21 | — | 35 |
| $CuCr_2O_4$ (I) | 300 | 106 | 31<br>(86)[c] | 11 |
| $ZrO_2$ (JM) | 300 | 0.008 | 0.008 | 0.012 |
| $ZrO_2$ (NL) | 300 | 0.006 | — | 0.012 |
| $\alpha$-$Al_2O_3$ | 300 | 0.003 | — | 0.003 |
| $\gamma$-$Al_2O_3$ | 300 | <0.001 | <0.001 | <0.001 |

[a] Rate normalized to 1% $O_2$, 1% CO, and no $H_2O$ added.

[b] Max reaction temperature prior to quenching to below the temperature at which the rates are measured.

[c] Heated in He + 2% $O_2$.

For the purpose of comparison, the activities of each of the metal oxides and supports were determined after successive increases in the pretreatment temperature. The results are shown in Table 2. The kinetics of the CO oxidation over the unsupported metal oxides have been reported in a previous communication to follow a power law over the same gaseous composition range used in this study (*7*):

$$\text{rate} = k p_{O_2}{}^{m} p_{CO}{}^{n} p_{H_2O}{}^{-l} \qquad (1)$$

with $m$, $n$ and $l$ usually fractional numbers. Based on these kinetic parameters the rates in Table 2 are all normalized to average (inlet and outlet) partial pressures of 1% $O_2$, 1% CO, with no $H_2O$ added to the inlet gas.

With the exception of $CuCr_2O_4$, the change in activity with high temperature treatment of these oxides is insignificant compared to those observed with the MX catalysts as shown in the next section. In the case of $CuCr_2O_4$, the activity decreased appreciably with increasing pretreatment temperature, but less so if heated in 2% $O_2$. Accelerated dissociation of this compound to $Cu_2Cr_2O_4$ and $Cr_2O_3$ in the reaction atmosphere could be the cause.

### *Mixed Catalysts with $ZrO_2$ or $\alpha$-$Al_2O_3$ as Supports*

The mixed powders of the active metal oxide (amo) and the support, hereafter

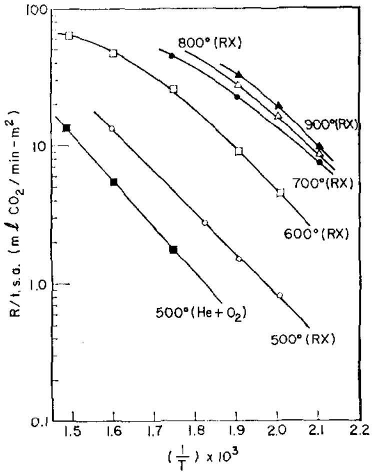

Fig. 1. Arrhenius plots for CO oxidation over CuO-$ZrO_2$(JM) (MX). Area ratio = 252, temperature on each curve, pretreatment temperature; RX = CO oxidation atmosphere.

designated as amo–$ZrO_2$ or amo–α-$Al_2O_3$ mixtures, for CO oxidation at a given testing temperature within the range of 200–400°C increased appreciably after the mixture was heated to a pretreatment temperature of higher than 500°C either in air or in the reaction atmosphere (RX), which was 1–2% CO and 1–2% $O_2$ at the inlet and 0.5–1% $O_2$ and 1–2% $CO_2$ at the outlet due to 100% conversion of CO at >500°C over most of the catalysts used. The increase in activity was greater with higher pretreatment temperature. A typical set of Arrhenius plots for a catalyst given successively increasing temperature pretreatment is shown in Fig. 1. The kinetics of CO and $C_3H_4$ oxidation over the mixed catalysts as well as the impregnated catalysts were found to obey Eq. (1), and the $m$ and $n$ values for the high temperature treated mixed catalysts are about the same for the various catalysts. They are $m \sim 0$ and $n \sim 0.8$–1. The rates reported are all normalized based on these kinetic parameters to 1% $O_2$, 1% CO, with no $H_2O$ added at the inlet. As seen in Fig. 1, the Arrhenius plots curved at high rates presumably due to the onset of mass transfer limitation. As the activity increased with heat treatment, lower testing temperatures were used to avoid this mass transfer limitation. This caused some difficulty in the quantitative comparison of the activation energies, and the extrapolation of the data to temperature outside the testing temperature range could have some degree of error. For this reason, the rate constants for these reactions are not derived, and the rates are compared at appropriately different temperatures for different active metal oxides to minimize extrapolation.

The activity changes as a function of the pretreatment temperatures for the $ZrO_2$ and α-$Al_2O_3$ supported MX catalysts are shown in Figs. 2 and 3, respectively. The ordinate, $R/R_0$, is the ratio of the measured catalytic reaction rate after heating to the pretreatment temperature to the calculated catalytic reaction rate of the initial mixture before heating, based on the reaction rates of the constituents and their surface areas given in Tables 1 and 2. The initial ratio of the surface area of the support to that of the amo (area ratio) is shown in parentheses next to the amo in the figures. The tem-

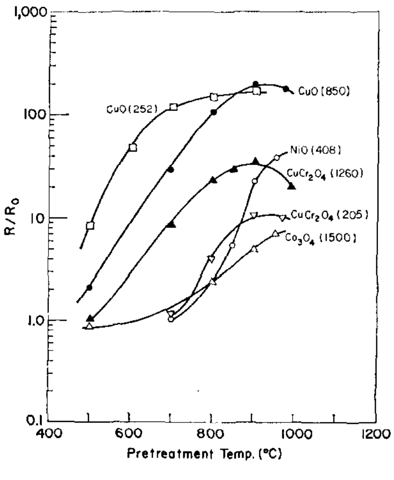

Fig. 2. CO oxidation over amo–$ZrO_2$ mixtures. Numbers in parentheses, area ratios, $R/R_0$ = activity after heating/activity before heating. All heating in CO oxidation atmosphere. CuO–$ZrO_2$ at 250°C, others at 300.

peratures at which the rates were taken are shown in the figure captions.

The results show that more than two orders of magnitude increase in $R/R_0$ are obtained after the MX catalysts are heated to 900°C. For the $CuO$–$ZrO_2$ mixtures considerable gain in activity is observed over the 500°C preheated samples. Unfortunately, changes at pretreatment temperatures less than 500°C could not be measured because of the necessity of cleaning the surface at 500°C prior to the rate measurements. In the vicinity of 900°C, maximum activity was obtained for most cases. Further increase in pretreatment temperature resulted in a decrease of activity. The maximum activities obtained at the indicated test temperatures with the heated mixtures are listed in Table 3. The activities are expressed as rate of $CO_2$ produced per unit total surface area ($R$/tsa).

Such rates of $C_2H_4$ oxidation over catalysts pretreated in the range of 800–900°C are listed in Table 3. The $C_2H_4$ oxidation rates were determined only over samples pretreated at the highest temperature of each series. As was observed for CO oxidation, the activity for $C_2H_4$ oxidation of the heated mixtures also was much higher than that observed for the unsupported metal oxides (*7*).

The surface areas of some of the catalysts before and after the heat treatment were determined and are listed in Table 4. Approximate corrections for the surface area changes were applied to the results given in Table 3.

### *Mixed Catalysts with γ-$Al_2O_3$*

γ-$Al_2O_3$ presintered at 850°C was used as a support for $CuO$, $Co_3O_4$ and $Cr_2O_3$. The activity of the $CuO$ and $Co_3O_4$ mixtures increased after each excursion to the high temperature and quenching to the test temperature, as was observed with the $ZrO_2$ and α-$Al_2O_3$ supported mixed catalysts. However, the activity gained on heating usually decreased rapidly and continually at constant catalytic reaction temperature. Therefore, quantitative oxidation rate results were difficult to obtain. The low activity of the γ-$Al_2O_3$ supported $Co_3O_4$ catalysts has been attributed to the formation of the $CoAl_2O_4$ spinel (*2*, *8*). The activities of two spinels, $CoAl_2O_4$ and $CuAl_2O_4$ were determined also. The results of the pretreated mixtures and of the spinels are shown in Table 5.

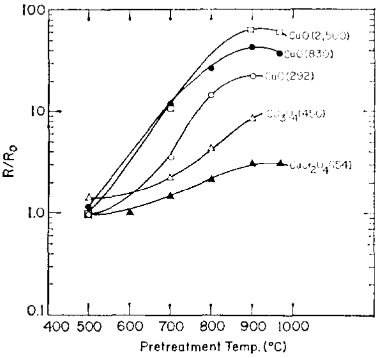

FIG. 3. CO oxidation over amo–α-$Al_2O_3$ mixtures. Numbers in parentheses = area ratios; $R/R_0$ = activity after heating/activity before heating. All heating in CO oxidation atmosphere. $CuO$–$ZrO_2$ at 250°C, others at 300°C.

### *Impregnated Catalysts*

The activities of the impregnated catalysts expressed as the rate of $CO_2$ produced per unit total surface area ($R$/tsa) are shown in Fig. 4 and are included in Tables 3 and 5. The compositions of the catalysts are expressed as micromoles of the active metal oxide per unit surface area of the support. The equivalent monolayer requirements are estimated to be 15–17 μmoles $CuO/m^2$-monolayer and 5–6 μmoles $Co_3O_4$ or $CuCr_2O_4/m^2$ monolayer.

## DISCUSSION

For a given mixed catalyst, the activity after heating at 900°C (800°C for some of

TABLE 3

Maximum Activity of the Heated Catalysts

| amo | Support | Type | wt% amo | A.R.[a] | Surface Concn[b] ($\mu$moles/m$^2$) | $T$ Pre-treatment[c] (°C) | $T$ Reaction (°C) | Rate [ml $CO_2$/min-m$^2$ (total)] | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | CO[d] | $C_2H_4$[e] |
| CuO | $ZrO_2$ | MX | 3.3 | 850 | | 900 (RX) | 250 | 11 | 0.020 |
| CuO | $ZrO_2$ | Imp. | 7.97 | | 100 | 900 (RX) | 250 | 9 | |
| CuO | $ZrO_2$ | Imp. | 4.8 | | 60 | 950 (RX) | 250 | 6.5 | |
| CuO | $ZrO_2$ (JM) | MX | 1.17 | 252 | | 900 (RX) | 250 | 32.2 | |
| CuO | $ZrO_2$ (JM) | MX | 6 | 46 | | 900 (RX) | 250 | 39 | |
| CuO | $ZrO_2$ (JM) | Imp. | 1.3 | | 163 | 800 (RX) | 250 | 33 | |
| CuO | $\alpha$-$Al_2O_3$ | MX | 1.13 | 2500 | | 900 (RX) | 250 | 1.6 | |
| CuO | $\alpha$-$Al_2O_3$ | MX | 3.36 | 830 | | 900 (RX) | 250 | 2.4 | |
| CuO | $\alpha$-$Al_2O_3$ | MX | 9.0 | 292 | | 900 (RX) | 250 | 3.4 | 0.026 |
| CuO | $\alpha$-$Al_2O_3$ | Imp. | 13.2 | | 165 | 800 (RX) | 250 | 14.4 | |
| $CuCr_2O_4$ (I) | $ZrO_2$ | MX | 3.1 | 205 | | 800 (RX) | 300 | 2.7 | |
| | | | | | | 800 (Air, 2 hr) | 300 | 3.0 | |
| | | | | | | 900 (RX) | 300 | 4.8 | |
| $CuCr_2O_4$ (I) | $ZrO_2$ | MX | 0.25 | 3000 | | 900 (RX) | 300 | 0.20 | |
| $CuCr_2O_4$ (I) | $ZrO_2$[f] | MX | 7.76 | 190 | | 800 (RX) | 300 | 4.5 | |
| | | | | | | 800 (air, 2 hr) | 300 | 3.8 | |
| $CuCr_2O_4$ (I) | $ZrO_2$[f] | MX | 1.17 | 1260 | | 800 (RX) | 300 | 2.9 | 0.018 |
| | | | | | | 800 (air, 2 hr) | 300 | 2.1 | |
| $CuCr_2O_4$ (II) | $ZrO_2$[f] | MX | 9.1 | 39 | | 500 & 800 (RX) | 300 | 6.4 | |
| | | | | | | 900 (20 hr) | 300 | 6.7 | |

TABLE 3 (continued)

| amo | Support | Type | wt% amo | A.R.[a] | Surface Concn[b] (μmoles/m²) | *T* Pretreatment[c] (°C) | *T* Reaction (°C) | Rate [ml $CO_2$/min-m² (total)] CO[d] | Rate [ml $CO_2$/min-m² (total)] $C_2H_4$[e] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 800 (RX) | 300 | | 0.02 |
| $CuCr_2O_4$ | $ZrO_2$[f] | Imp. | 11.0 | | 17 | 700 (air, 20 hr) | 300 | 1.8 | |
| | | | | | | 900 (air, 20 hr) | 300 | 1.8 | 0.027 |
| $CuCr_2O_4$ | $ZrO_2$[f] | Imp. | 6.76 | | 10.4 | 900 (RX) | 300 | 1.7 | |
| $CuCr_2O_4$ | $ZrO_2$ | Imp. | 0.94 | | 4.7 | 900 (RX) | 300 | 1.33 | 0.011 |
| | | | | | | 900 (RX) | 300 | 2.00 | |
| $CuCr_2O_4$ | $\alpha$-$Al_2O_3$ | MX | 4.04 | 154 | | 900 (RX) | 300 | 2.08 | |
| | | | | | | 900 (air, 20 hr) | 300 | 1.69 | 0.006 |
| $Co_3O_4$ | $ZrO_2$ | MX | 1.5 | 1500 | | 900 (RX) | 250 | 0.8 | |
| $Co_3O_4$ | $ZrO_2$ | Imp. | 3.74 | | 46 | 900 (RX) | 250 | 4.6 | |
| $Co_3O_4$ | $\alpha$-$Al_2O_3$ | MX | 4.56 | 450 | | 900 (RX) | 250 | 1.1 | |
| | | | | | | 900 (air, 2 hr) | 250 | 1.2 | |
| NiO | $ZrO_2$ | MX | 7.73 | 408 | | 980 (RX) | 300 | 0.18 | |
| | | | | | | 900 (air, 2 hr) | 300 | 0.20 | |
| NiO | $ZrO_2$ | Imp. | 2.76 | | 36 | 800 (RX) | 300 | 0.20 | |

[a] A.R. = starting surface area of support/starting surface area of amo (mixed catalysts).

[b] μmoles of amo/m² of starting surface area of support (impregnated catalysts).

[c] Maximum temperature the catalyst subjected prior to rate quoted; (RX) in reaction stream; (air) in furnace.

[d] Rate normalized to 1% $O_2$, 1% CO, no $H_2O$ added. Some values are extrapolated, approx area change due to heating corrected.

[e] Rate normalized to 1% $O_2$ 0.1% $C_2H_4$, no $H_2O$ added.

[f] $ZrO_2$ preheated at 700°C.

TABLE 4

Surface Area of Mixed Catalysts

| Catalyst | Surface area ($m^2/g$) | |
|---|---|---|
| | Before heating | 900°C 2 hr |
| $CuO$–$ZrO_2$ (3.3%) | 10.3 | 7.8 |
| $CuO$–$ZrO_2$ (JM) (6%) | 1.0 | 0.94 |
| $CuCr_2O_4$–$ZrO_2$ (3.0%) | 10.2 | 10.1 |
| $Co_3O_4$–$\alpha$-$Al_2O_3$ (4.5%) | 10.1 | 8.8 |
| $Cr_2O_3$–$\gamma$-$Al_2O_3$ (6.4%) | 93 | 87 |
| $Co_3O_4$–$\gamma$-$Al_2O_3$ (13%) | 91 | 91 |
| $CuO$–$\alpha$-$Al_2O_3$ (3.3%) | 10.5 | 9.5 |

the samples) in a stream of He containing an inlet concentration of 1% $O_2$ and 1% CO for a duration of 20–30 min is approximately the same as that after heating in air at the same temperature for 1–2 hr. Repetition of the heat treatment at the same temperature for longer time results in only small improvement. This suggests that the rate to reach a certain state of activity is relatively fast. The activity is strongly dependent on the pretreatment temperature for these catalysts. The presence of CO and $CO_2$ and the partial pressure of $O_2$ makes little difference in the degree of enhancement in activity by heating.

Figure 5 shows the activities of the $CuO$–$\alpha$-$Al_2O_3$ (MX) catalysts. The $R$/tsa value increases with increasing CuO concentration in the catalysts and approaches a constant value at high CuO concentration. The activity per initial amo surface area, as measured by $R/R_0$, decreases with increasing CuO concentration. This behavior is typical for both types of catalysts studied. Similar results have been reported for a dilute solid solution of NiO–MgO (*9*) and for CuO supported on $Al_2O_3$ (*10*).

Yao and Bettman (*9*) studied the chemisorption of NO and CO on $Co_3O_4$ supported on $ZrO_2$ (prepared by impregnation) and concluded that $Co_3O_4$ exists in this catalyst in two different phases. Upon heating a catalyst of very low Co concentration to 500°C or above, $Co_3O_4$ spreads over the $ZrO_2$ surface to form a two-dimensional dispersed phase which was found to be relatively inactive for $C_2H_4$ oxidation. If the surface concentration of $Co_3O_4$ is

TABLE 5

Activity of Heated $\gamma$-$Al_2O_3$ Supported Catalysts

| Catalyst | Pretreatment | $T$ Reaction (°C) | $R$/tsa[a] [ml $CO_2$/min-$m^2$ (total)] |
|---|---|---|---|
| $CuO$–$\gamma$-$Al_2O_3$ (MX)<br>8.82%<br>A.R. 2700 | 900°C(RX) | 250 | 0.35 |
| $CuAl_2O_4$[b] spinel | 500°C He + 1% $O_2$ | 250 | 0.9 |
| $Co_3O_4$–$\gamma$-$Al_2O_3$ (MX)[c]<br>10% | 600°C, air 24 hr | 250 | 0.125 |
| A.R. 670 | 850°C air 24 hr | 250 | 0.58 |
| $Co_3O_4$–$\gamma$-$Al_2O_3$ (Imp)[d] | 600°C air 24 hr | 250 | 0.16–0.001 |
| | 850°C air 24 hr | 250 | 0.06–<0.001 |
| $CoAl_2O_4$[e] spinel | 500°C, He + 2% $O_2$ | 300 | 0.003 |
| $Cr_2O_3$–$\gamma$-$Al_2O_3$ (MX)<br>6.44%<br>A.R. 1175 | 900°C(RX) | 300 | <0.001 |

[a] Normalized to 1% $O_2$, 1% CO, no $H_2O$ added.

[b] See Ref. (*1*) for preparation, area 11.8 $m^2/g$.

[c] See Ref. (*7*) for preparation, $Co_3O_4$ and $\gamma$-$Al_2O_3$ presintered at 850°C.

[d] See Ref. (*7*) for preparation; activity dependent on method of preparation.

[e] See Ref. (*7*). Area 11.3 $m^2/g$.

higher than 7 μmoles Co/m$^2$ of $ZrO_2$, a second phase similar to that of bulk $Co_3O_4$ starts to form. These two phases are called the δ-phase for the two-dimensional dispersed phase and the β-phase for the three-dimensional particles, after O'Reilly and MacIver (*11*). In this study there was no experimental information on the surface concentration of the amo in the catalysts, but the activity results obtained are in agreement with the spreading and the two-phase model. During the high temperature treatment, the active metal ions migrate over the support surface driven by the concentration gradient at the interface and thus increase the amo surface. As the concentration of amo increases, the surface becomes saturated with the δ-phase; consequently a larger fraction of the active metal ions would exist as the crystalline oxide (β-phase). The total number of active metal ions on the surface would be higher with greater loading of the amo up to the point where the growth of the β-phase particles becomes the limiting factor. In general, the specific activities of the β- and δ-phases can be very different from that found on the $Co_3O_4$–$ZrO_2$ catalysts.

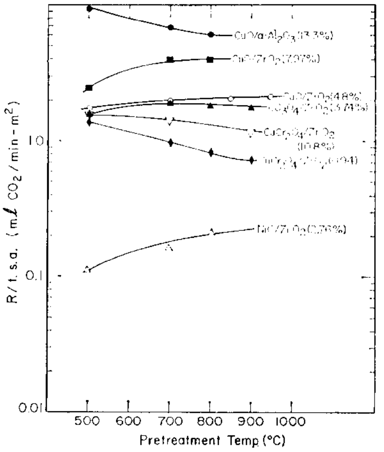

FIG. 4. CO oxidation over impregnated catalysts. Number in parentheses, wt% of amo, CuO and $Co_3O_4$ catalysts at 200°C, $CuCr_2O_4/ZrO_2$ at 250°C, $NiO/ZrO_2$ at 300°C.

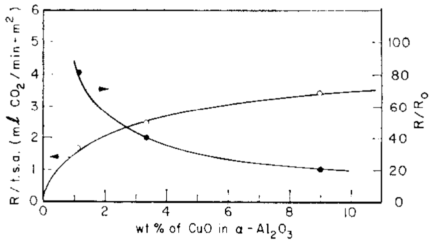

FIG. 5. CO oxidation over $CuO$–α-$Al_2O_3$ at 250°C, $R$/tsa in ml of $CO_2$/min-m$^2$ (total) and $R/R_0$ = activity after heating/activity before heating vs wt% of CuO in the mixed catalysts.

This is true for some of the systems used in this work and is discussed below.

It is evident from the activity of CuO and $CuCr_2O_4$ on $ZrO_2$ supports of different surface area that the area ratio of the support to the active metal oxide is a more important parameter in determining the activity values than the weight percentage of the amo. Although the results shown in Table 3 lack a uniform basis of area ratio for quantitative comparison, qualitatively one can conclude that the activity of the two types of catalysts, mixtures and impregnated, for each amo–support couple are quite comparable, at least in the high amo concentration region. This implies that the same activity state was approached either from heating a mechanical mixture to high temperature or from impregnation followed by calcination. The latter starts in a more dispersed state and requires lower temperature heating to reach the same degree of spreading.

It was observed that if the catalyst mixtures were allowed to cool down slowly from the high pretreatment temperature instead of quenching, the activity gain, $R/R_0$, would be smaller. This effect is particularly pronounced for samples with low amo concentration. A possible explanation of the deactivation during slow cooling is the diffusion of the active metal ions into the interior of the support by local exchange between the active metal ions with the cations of the support (*12*).

### *$CuO$–$ZrO_2$, α-$Al_2O_3$ Couples*

Of the catalysts listed in Table 3, both MX and impregnated, $CuO$–$ZrO_2$ are the only couple exhibiting activity per total surface area approaching that of the unsupported active oxide (45–50 ml $CO_2$/min-m$^2$ of CuO at 250°C). The sample with an initial area ratio of 850, which has a total loading equivalent to about 2.5 monolayer of the support, is expected to have a large fraction of the CuO in the δ-phase after spreading at high temperature. The overall activity per unit total surface area of about $\frac{1}{4}$ of that for the unsupported CuO indicates that the activity of the δ-phase of CuO on $ZrO_2$ is comparable to that of CuO. This is much higher than that reported for the δ-phase of $Co_3O_4$ on $ZrO_2$ (*8*). Whether the apparent higher activity of the catalysts made using $ZrO_2$ (JM) than those using $ZrO_2$ (National Lead Co.) are due to a lower area ratio or the chemical nature of the $ZrO_2$ used is not clear.

The activity per total surface area of the $CuO$–α-$Al_2O_3$ (MX) catalysts are about $\frac{1}{4}$ of CuO supported on $ZrO_2$ of the same area ratio. An increase in activity of 60-fold after 900°C heating was observed for the sample with an area ratio of 2500, which contains CuO equivalent to about a monolayer on the α-$Al_2O_3$. This suggests that the δ-phase of CuO on α-$Al_2O_3$ is also quite active. It is not known whether the lower activity of $CuO$–α-$Al_2O_3$ (MX) compared with $CuO$–$ZrO_2$ is due to slower spreading of CuO over α-$Al_2O_3$ or lower intrinsic activity of the δ-phase on α-$Al_2O_3$. The fact that $CuO$/α-$Al_2O_3$ prepared by impregnation, which has a high loading equivalent to about 11 monolayers, gave an overall activity similar to that obtained on the $ZrO_2$ supported CuO favors the former proposition of slower spreading on α-$Al_2O_3$.

### *$Co_3O_4$–$ZrO_2$, α-$Al_2O_3$ Couples*

The results on $Co_3O_4$ mixed catalysts shown in Figs. 2 and 3 and Table 3 support the contention reported previously (*8*), that $Co_3O_4$ can spread over the support surface to give an increase in $R/R_0$. But the activity of the δ-phase, a major component for the sample with an area ratio of 1500, is much lower than that of $CuO$–$ZrO_2$ (MX) even though $Co_3O_4$ is by itself much more active than CuO. The higher loading in the impregnated sample is beneficial, but the overall activity is still far below that of the unsupported $Co_3O_4$ (by a factor of over 20). α-$Al_2O_3$ is no better support for $Co_3O_4$ than $ZrO_2$.

### *$NiO$–$ZrO_2$ Couple*

The activity of $NiO$–$ZrO_2$ (MX) increases by a factor of about 30 after 900°C heating. The $R$/tsa for the heated mixed catalyst and that prepared by impregnation is about the same, and about 10% of the unsupported NiO specific activity.

### *Supported $Cr_2O_3$ Catalysts*

The measured activities of both $ZrO_2$ and α-$Al_2O_3$ supported $Cr_2O_3$ MX catalysts are very close to those of the supports alone. Therefore, the results are experimentally inaccurate and very susceptible to traces of impurity on the surface. In view of the fact that the activity of $Cr_2O_3$ itself is very low for the reaction studied, the failure to observe measurable net rate changes does not necessarily mean that there is no change in activity due to the high temperature treatment. Indeed a fast and distinctive change in the color of the supported $Cr_2O_3$ catalysts was observed after the high temperature treatment, the same as that observed on the other catalysts.

### *$CuCr_2O_4$–$ZrO_2$, α-$Al_2O_3$ Couples*

The results on the supported $CuCr_2O_4$ catalysts are more difficult to resolve because of the following complications: (a) Because of the thermal instability of $CuCr_2O_4$, one sample of it was preheated only to 700°C ($CuCr_2O_4$ II). MX catalysts prepared from it reached a high activity after heating at 500°C. Heating the mixture to above 700°C could cause sintering and decomposition of the $CuCr_2O_4$ to an unknown degree even though the $R$/tsa after 900°C appeared nearly the same as that after 500–800°C for the particular mixture studied. (b) $CuCr_2O_4$(I) was prepared by heating (II) to 900°C and the XRD showed the presence of minor amounts of $Cu_2Cr_2O_4$ and $Cr_2O_3$. The contribution of each of these components to the spreading and the activity cannot be resolved. (c) Successive heat treatment of a sample of unsupported $CuCr_2O_4$ (I) in the reaction atmosphere caused deactivation as shown in Table 2. The effect of the support on the deactivation process, if any, is not known. The results in Figs. 2 and 3 were calculated based on the original activity (500°C preheated in Table 2). (d) The catalyst prepared by impregnation was shown by XRD to be $CuCr_2O_4$, but the results are not sufficiently accurate to exclude the presence of other compounds. Despite all these difficulties, the supported $CuCr_2O_4$ catalysts show the same general patterns observed over the other amo–support couples, such as increasing activity with increasing temperature of heating the MX catalysts, the area ratio effect, the similarity between $ZrO_2$ and $\alpha$-$Al_2O_3$ as support, the same activity level achieved by the heated mixtures and the impregnated catalysts, and the readiness to reach each activity state.

### $\gamma$-$Al_2O_3$ *as Support*

The $\gamma$-$Al_2O_3$ supported catalysts are less active per unit total surface area than their corresponding catalysts supported on $ZrO_2$ or $\alpha$-$Al_2O_3$. $CuAl_2O_4$ is comparatively more active per unit surface area than a CuO–$\gamma$-$Al_2O_3$ mixture which had gone through three 900°C heating and quenching cycles. The rates of the latter were taken after the deactivation with time almost ceased. Shelef *et al.* (*13*) examined the surface of $CuAl_2O_4$ (same source as that used in this study) with ion scattering spectrometric technique and found that over 60% of the surface cations are Cu instead of Al. Therefore, it can be inferred that the Cu ion concentration on the $CuAl_2O_4$ surface is high but the intrinsic activity of Cu ions on the spinel surface are less than those on $ZrO_2$ or $\alpha$-$Al_2O_3$, and much higher than that of Co in $CoAl_2O_4$. Misra and Chaklader (*14*) reported the formation of $CuAl_2O_4$ spinel upon heating a CuO and $\gamma$-$Al_2O_3$ mixture to 800°C or higher. If Cu on the surface of the heated CuO–$\gamma$-$Al_2O_3$ mixture is in the form of the spinel, then the lower $R$/tsa of the mixture than that of $CuAl_2O_4$ suggests that the Cu concentration on the surface of the mixture is less than half of a monolayer. This is not unexpected because in the first place there is a low concentration of CuO in the mixture (equivalent monolayer) and in addition the Cu ions diffuse into the $Al_2O_3$ to form bulk spinel. This was evidenced by the slow deactivation of the catalyst.

The very low activity of $Co_3O_4$–$\gamma$-$Al_2O_3$ (Imp) is approximately equal to that of $CoAl_2O_4$ and confirms the supposition that $\gamma$-$Al_2O_3$ deactivates the $Co_3O_4$ via spinel formation. The $Co_3O_4$–$\gamma$-$Al_2O_3$ (MX) made from 850°C presintered $Co_3O_4$ and $\gamma$-$Al_2O_3$ became more active after 24 hr heating at 850°C (about 4 times), but still was far less active than that supported on $ZrO_2$ or $\alpha$-$Al_2O_3$. This could be explained as follows: The $\gamma$-$Al_2O_3$ after heating at 850°C appeared under electron microscope as amorphous aggregates (*2*) possessing large internal surface area and pores. Therefore, the contact between the $Co_3O_4$ (presintered at 850°C) and the presintered $\gamma$-$Al_2O_3$ could be so poor that reaction to form $CoAl_2O_4$ is slow. Migration of Co to some $\alpha$-$Al_2O_3$ formed from the $\gamma$-$Al_2O_3$ after the long time heating at 850°C could enhance somewhat the activity of the mixed catalyst. The activity of the $Cr_2O_3$ supported on $\gamma$-$Al_2O_3$ was again too low to be meaningful.

The fact that the activity of amo–$\gamma$-$Al_2O_3$ mixtures increased immediately after each high temperature treatment and quenching to the testing temperature suggests that the active metal ions could spread over the $\gamma$-$Al_2O_3$ surface the same as that observed over $ZrO_2$ and $\alpha$-$Al_2O_3$. The slow deactivation at the testing temperature for the $\gamma$-$Al_2O_3$ supported catalysts could be visualized as follows: the quenched surface is covered with a large number of the active metal ions in the $\delta$-phase which apparently continue to react with the support surface at the testing temperature to form the less active spinels. This implies that the activation energy for spreading is greater than that for reaction to form the spinels. However, we cannot supply proof for such speculations at this time. Further work is definitely needed for the understanding of these processes.

## CONCLUSION

The effective surface area of an active metal oxide catalyst for high temperature use can be extended by supporting it on a less active oxide of higher surface area provided that the amo is thermally stable and there is no interaction with the support to form grossly less active surface compounds. The supported catalyst can be prepared either by a conventional impregnation–calcination method or by heating a mixture of the finely divided amo with the support to 800°C or above. The improvement achievable is highly dependent on the nature of the amo and that of the support. For the catalysts included in this work, CuO supported on $ZrO_2$ has the highest potential improvement factor over the use of pure CuO. In order to maintain the activity at high temperature for relatively long time, large excess of CuO over that required for monolayer formation on the $ZrO_2$ must be used to compensate for any loss due to diffusion into the bulk.

If the limiting factor is the size or total weight of the catalyst, then the improvement factor realizable for a catalyst to be used at a 900°C maximum temperature is governed by the specific surface area ratio of the support and the amo. For the CuO–$ZrO_2$ couple, the surface area values are 10 $m^2/g$ $ZrO_2$ and 0.35 $m^2/g$ CuO after 900°C calcination. The maximum improvement in oxidation activity compared to that of pure CuO (on the same weight basis) is then 7. By virtue of the higher surface area of $\gamma$-$Al_2O_3$ (80–100 $m^2/g$) the activity of CuO–$\gamma$-$Al_2O_3$ (MX) after 900°C calcination is twice that which would be obtained if the weight of CuO were used. Indeed CuO/$\gamma$-$Al_2O_3$ (prepared by impregnation) has been widely studied as a potential catalyst for removing CO from the automotive exhaust (*15*, *16*). The potential improvement factors for the other couples reported in this paper are less.

When one considers the CO oxidation activity alone, CuO or $CuCr_2O_4$ mixed with or impregnated on $ZrO_2$ or $\alpha$-$Al_2O_3$ in addition to CuO–$\gamma$-$Al_2O_3$ catalysts have the potential to be useful for automotive emission control. Attempts to apply these catalysts supported on monolithic substrate for automotive exhaust purification have been made by the authors and reported elsewhere (*17*). In such applications the impregnation method is favored due to the poor adherence of the mixed sintered powders to the substrate, however, the active metal oxide loading is usually so high that the existence of separate active metal oxide phase and its spreading over the wash-coat surface during the high temperature operation undoubtedly plays an important role for the durability of the catalysts.

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