CO Oxidation on α-Alumina-Supported Chromia Catalysts

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Data relating to the activity in CO oxidation of α-alumina-supported chromia catalysts under both dry and H_2O-inhibited conditions and after extended heat treatment in O_2 are presented in this paper. The possible effect of different reductive and thermal activation procedures are also investigated. Gas adsorption and X-ray diffraction analysis are employed to suggest an interpretation of differences in catalytic activity based on different types of surface Cr entities. We found that α-alumina-supported Cr exhibited specific activity higher than that of bulk Cr_2O_3 and far superior to that of γ-alumina-supported forms.

INTRODUCTION

CO oxidation is a reaction of general environmental importance, specifically relevant to the automobile exhaust pollution control problem. The replacement of currently employed noble metal catalytic systems by base metal oxides presents considerable economic incentives while posing technical problems of an as yet unresolved nature, some of which are detailed in the work of Kummer (1).

Two considerations that are of critical importance in the selection of suitable base metal oxide catalysts are the resistance to sulfur poisoning and the activities displayed toward the relevant reactions. Cr_2O_3 in its unsupported form has been shown to compare favorably with other base metal oxides in respect to sulfur poisoning, both in actual poisoning studies (2) and by way of an appreciably lower sulfate decomposition temperature (1), a theoretical measure of the ease of activity

regeneration following poisoning. Further, the infrared spectroscopic and kinetic studies of Hertl and Farrauto (3) indicate that the susceptibility of the otherwise successful unsupported copper chromite catalysts to SO_2 poisoning is in large measure attributable to the Cu and not the Cr component.

A comparison of the specific activity of the common unsupported metal oxides (1) yields, however, quite another picture. Cr_2O_3, a detailed kinetic evaluation of which has been carried out by Yu Yao (4), shows considerably less specific activity as compared to other metal oxides. If Cr_2O_3 is to find use in a catalyst formulation for pollution control applications, it would still be necessary to seek a suitably supported form of the oxide, with increased surface area and thermal stability *and* greater activity.

Data on CO oxidation over supported chromia appear to be limited to that of Bridges *et al.* (5) who used CO oxidation activity as a check on other measures of

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TABLE 1

α-Al$_2$O$_3$ Properties

Pellet size	$\frac{3}{16}$ in.
BET area	5.3 m^2/g
Range of pore radii	4000–300 Å
Total pore volume	0.27 ml/g
Pellet density	1.9 g/cm^3
Percentage SiO$_2$	0.13
Percentage Na$_2$O	0.083
Mean crystallite size	>2000 Å

chromia area in impregnated γ-alumina catalysts of up to 10 wt% Cr and that of Yu Yao and Kummer (6) who studied heat-treated mixtures of Cr$_2$O$_3$ with refractory supports. Although both reported minimal activity in this reaction, the results are far from conclusive in view of the known complexity of chromia-support interaction.

A voluminous literature relating to chromia–alumina catalysts (mainly to the high area γ-type alumina) attests to the catalytic importance heretofore attached to these systems. Poole and MacIver in a comprehensive review of these results (7) point to the great differences between such supported chromias and bulk Cr$_2$O$_3$, as in the observation that in a series of such catalysts, prepared by impregnation, the X-ray diffraction lines of Cr$_2$O$_3$ were remarkable by their absence until very high (≃25 wt%) Cr loadings were attained. Further, Deren et al. (8) and Matsunaga (9) indicate that under oxidizing conditions most of the Cr in such support configurations may in fact be present in a significantly higher oxidation state than the +3 of bulk Cr$_2$O$_3$.

There is no evidence in the literature that any chromium entity other than Cr$_2$O$_3$ advantageously catalyzes CO oxidation. The use of a low area support such as α-Al$_2$O$_3$ which is, incidentally, isostructural with Cr$_2$O$_3$, could conceivably result in the formation of surface entities more favorable to CO oxidation than the hitherto examined cases.

EXPERIMENTAL

Apparatus. Kinetic data were obtained in a spinning basket type gradientless CSTCR (continuous stirred tank catalytic reactor). Analytic systems employed to quantify feed and product streams included a Beckman Model 315A continuous infrared analyzer for CO$_2$ and a Carle Model AGC 111 gas chromatograph. A more detailed description of the equipment has been given elsewhere (11).

A second unit designed for the measurement of gas adsorption via a continuous flow-pulse injection technique was used to study the chemisorptive characteristics of the catalysts and also served as a catalyst preparation unit. Research and Ultra-High Purity grade gases were always employed in these measurements. Again a more detailed description can be obtained elsewhere (11).

X-Ray diffraction results were obtained from finely powdered samples of the catalyst on a Norelco powder diffractometer equipped with a graphite crystal monochromator using copper Kα radiation.

Catalysts. Catalysts were prepared by impregnating $\frac{3}{16}$-in. pellets of α-Al$_2$O$_3$ (Type T-708, Girdler Chemicals) to incipient wetness with a solution of chromic anhydride (CrO$_3$) of the required concentration. The manufacturer-supplied data on the α-Al$_2$O$_3$ support are shown in Table 1. The wet impregnated pellets were dried for 15 hr at 383 K in air and for a further 2 hr in argon at 473 K before reduction for 8 hr at 773 K in 20% H$_2$/Ar. The reductive activation step was carried out in one instance by a 20% CO mixture and in another, Ar itself was employed to provide a purely thermal activation of the catalyst. Subsequent to reduction the catalysts were degassed for 2 hr at 773 K in pure Ar. Catalysts so prepared are described hereafter by the weight percent Cr metal content without specifying the oxidized state of the metal.

The heat-treated catalysts are those that after preparation were treated for 20 hr at 973 K in O_2 followed by reduction (H_2) and degassing at 773 K for 2 hr each.

Procedures. Rate data were obtained for all catalysts in the temperature range 460 to 540 K for both non-heat-treated and heat-treated catalysts under dry and H_2O inhibited conditions for the former, and under only dry conditions for the latter. A 5.21 vol% CO in air mixture was employed in all cases except for the non-heat-treated 1% Cr and for α-alumina itself both of which due to low activity required higher CO percentages (10 and 12 vol%) to yield reliable rate measurements at the lower temperatures. For the H_2O-inhibited conditions the feed contained, in addition to CO and Air, 2.5 vol% H_2O. Reaction orders in O_2 and CO pressures were also obtained for eacy of the catalysts.

Procedures were as follows: Reaction was in every case preceded by 2 hr pretreatment in air at 523 K. Following a preliminary estimation of the dry activity of the catalyst, a series of runs were carried out, under both H_2O inhibited and dry conditions. These consisted of a run at constant temperature and increasing CO concentration and two runs at increasing temperatures and constant feed compositions in air and O_2, respectively. The latter yielded rate vs temperature relations as also a nominal reaction order in O_2 pressure. After measurements under H_2O-inhibited conditions, the catalyst was dried at 523 K and dry rate data were then obtained. It was found that the original dry activity of the catalyst was fully recovered by the removal of H_2O from the feed stream.

Data so obtained showed good reproducibility and we found no significant catalyst "self-deactivation" (*4*). Our measured temperatures were that of the bulk gas environment; however, estimates based on observed rates (*12*) indicated no diffusion limitation and an intrapellet gradient not greater than a few degrees K.

Gas adsorption and X-ray diffraction measurements were made in all cases on catalyst pellets that had been used in reaction measurements and had been ground to a powder of fine consistency. Standard pretreatment prior to pulsing adsorbable gases consisted of heating in O_2 at 523 K for 1 hr and subsequent reduction at 773 K in 20% H_2/Ar for 1 hr. Finally the catalyst was degassed at this temperature in Ar for 2 hr and cooled down to the temperature at which adsorption was to be measured. Pulses of the desired gas (H_2, O_2, or CO) were injected and uptakes were measured. Extensive experimentation on the lowest and highest loading catalysts confirmed good reproducibility for the adsorption measurements at 298 K. Some difficulty was experienced in obtaining equally reproducible data at the higher temperatures (523 K).

RESULTS

Kinetics and Activity

Oxidation kinetics over base metal oxides have been usually reported (*6*) by means of a power law expression of the form:

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

All our catalysts displayed a first-order dependence on CO percentage in both the dry and H_2O inhibited cases, so that $n = 1$ in all cases. This is in agreement with reaction orders found by other workers (*5*).

The nominal O_2 reaction order obtained from comparison of activity in air and O_2 at 523 K presented interesting variations. The reaction order m varied under dry conditions from $+0.37$ for the 1% Cr to -0.16 for the 3.38% Cr catalyst. It may be noted that one of the characteristics unique to bulk Cr_2O_3 among base metal oxides in CO oxidation is a negative fractional order in O_2 pressure (*4*). O_2 reaction order in H_2O-inhibited rates was in all cases positive, but ranged from $+0.6$ on 1% Cr to $+0.1$ on 5.21% Cr.

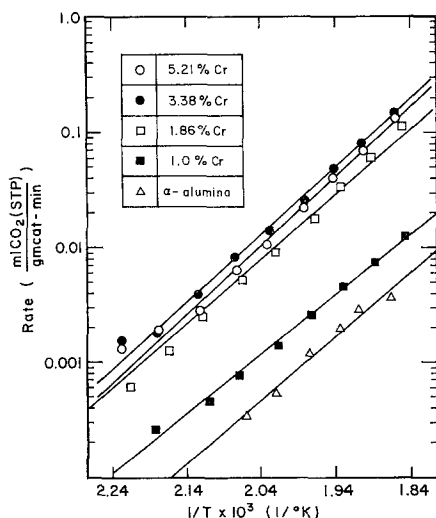FIG. 1. Normalized rates vs inverse temperature for H₂O-free conditions, on H₂-activated catalysts.

Measurements of rates on α-Al₂O₃ itself, necessary for purposes of comparison, required the use of high CO concentrations in the feed. All rate data were therefore normalized to that of a 1 vol% CO in Air.

Figure 1 displays an Arrhenius-type plot of the normalized rate vs temperature relationship obtained on the fresh catalysts and the α-Al₂O₃. Note that the transition from
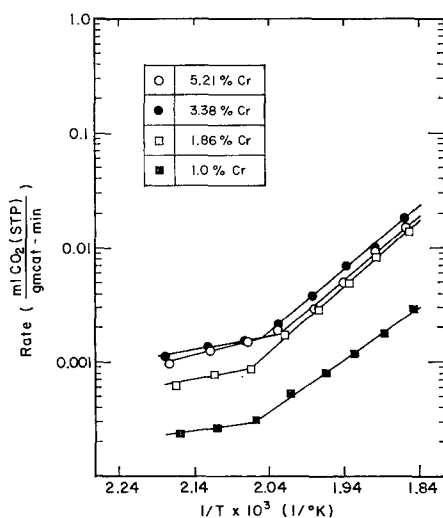
1 to 1.86% Cr is marked by a large increase in activity. Linearity in this and further figures is for the most part good and the straight lines drawn indicate least square fits. Figure 2 shows the H₂O-inhibited activity of the same series of catalysts. In this and other H₂O-inhibited rates two temperature regions of different activation energies prevailed. As for the case of dry reaction conditions, the activity of the 1.86% and higher Cr loading catalysts is significantly higher than the activity of the 1% Cr catalyst. Also, in both the dry and H₂O-inhibited cases, the effect of increased Cr loading on activity appears to have leveled off and, in fact, the 5.21% Cr shows less activity than the 3.38% Cr.

Rates obtained on the heat-treated catalysts are shown in Fig. 3. Heat treatment produced a large increase in the activity of the 1% Cr, while all other loadings suffered some small diminution in activity. The heat-treated 1.86% Cr catalyst now showed activity slightly lower than that of the 1% Cr catalyst. Also pertinent is the fact that in their final heat-treated forms, catalysts of widely differing Cr
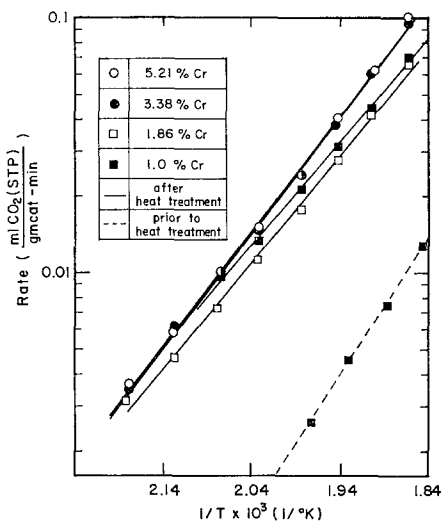

FIG. 2. Normalized rates vs inverse temperature for H₂O-inhibited conditions, on H₂-activated catalysts.

FIG. 3. Normalized rates vs inverse temperature for H₂O-free conditions, on heat-treated H₂-activated catalysts.

loadings showed no striking differences in activity.

Finch (13), in studies of supported chromic anhydride, pointed to the existence of substantial differences between reduction profiles obtained in H_2 and CO. To investigate the possible significance of these to catalyst activity, we prepared two further 5.21% Cr catalysts, one activated by CO reduction and the other by a purely thermal process as described previously. Dry and H_2O-inhibited reaction rates obtained on these catalysts together with that of the regular H_2 reduced one are shown in Fig. 4. It is seen that even though the CO-reduced and thermally activated catalysts appear to possess better activity, the dry and H_2O-inhibited activities of all three bear substantially the same relationship to each other, indicating similar susceptibilities to H_2O inhibition on the part of the CO reduced and thermally activated catalysts.

Rate data were also obtained on a 13% Cr catalyst supported on γ-alumina of area 192 m^2/g using a separate differential reactor. This catalyst showed activity comparable to that of the non-heat-treated 1.86% Cr/α-Al_2O_3 catalyst.

Gas Adsorption Data

Powdered samples of each of the catalysts and α-Al_2O_3 of weights between 0.5 and
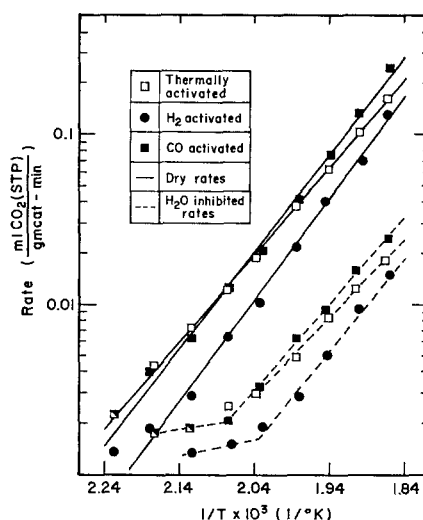

FIG. 4. Comparison of normalized rates vs inverse temperature relationships on 5.21% Cr catalysts activated thermally and in H_2 and CO; H_2O-free and inhibited conditions shown.

1.5 g were employed in gas adsorption measurements. Pretreatment procedures prior to these measurements were as detailed previously. Table 2 lists the O_2 and CO uptakes per gram of catalyst for each case studied.

O_2 adsorption was irreversible and no temperature-programmed desorption was obtained up to temperatures of 973 K. At 523 K O_2 uptake was greater than at 298 K on all catalysts, but more so on the 1% Cr

TABLE 2

Gas Adsorption Data

Catalyst	O_2 μl(STP)/g·cat at 298 K	O_2 μl(STP)/g·cat at 523 K	O_2 μl(STP)/g·cat at 298 K after heat treatment	CO μl(STP)/g·cat at 298 K	
				Total[a]	Irreversible[b]
1.0% Cr	65.07	116.91	135.97	77.75	25.61
1.86% Cr	106.84	174.23	154.21	125.28	48.37
3.38% Cr	108.39	202.72	178.15	152.67	73.68
5.21% Cr	171.02	188.71	143.90	186.46	97.86
13.0% Cr on γ-alumina	3.16×10^3	—	—	—	—

[a] Volume adsorbed with injections at 3-min intervals; see text.
[b] Obtained from difference of total adsorption and readsorption after 1 hr.

TABLE 3

X-Ray Diffraction Results

Catalyst	Intensity ratio[a] $\dfrac{I_{Cr_2O_3}}{I_{Al_2O_3}} \times 10^2$	Crystallite size[b], d (Å)
1.0% Cr	0.0	—
1.86% Cr	1.73	210
3.38% Cr	3.80	161
5.21% Cr	5.66	338
1.0% Cr heat treated	1.86	304
1.86% Cr heat treated	2.46	577
3.38% Cr heat treated	5.80	701
5.21% Cr heat treated	8.46	524

[a] Integrated intensity of Cr_2O_3(104) X-ray diffraction line, normalized with respect to intensity of Al_2O_3(104) line.

[b] Cr_2O_3 crystallite size as calculated from X-ray line (104) broadening at half peak intensity.

reflecting perhaps greater oxidizability of the Cr on this catalyst. The O_2 uptakes at 298 K of the heat-treated catalysts increased in all cases except the 5.21% Cr catalyst, but there was a considerable narrowing of differences as compared to the non-heat-treated catalysts. It should be noted that because of the relatively high temperatures at which such uptakes were measured, O_2 adsorption does not correlate with chromia surface area. The uptake on the 13% Cr/γ-alumina catalyst was much higher than that on the other catalysts as expected from the data of Bridges et al. (5).

CO adsorption on the catalysts was in large measure reversible, and the pulse injection technique is applied only with difficulty to such systems (14). We termed, loosely, the volume uptake upon injection at 3-min intervals and the volume undesorbed after 1 hr as "total" and "irreversible" uptakes, respectively (Table 2).

X-Ray Diffraction

Powder diffractometry of each catalyst and α-Al_2O_3 yielded valuable information. All catalysts except the 1% Cr showed clear diffraction lines due to Cr_2O_3 in addition to those of α-Al_2O_3. The 1% Cr showed no lines due to Cr_2O_3 prior to heat treatment, but after such treatment showed well-defined lines due to crystalline Cr_2O_3. In all cases the only lines observed were that of α-Al_2O_3 and the isostructural Cr_2O_3.

We computed two quantities, a ratio of the integrated intensity of the Cr_2O_3 (104) line to that of the adjacent α-Al_2O_3 (104) line and a mean Cr_2O_3 crystallite size, in each case. The first ratio is, in the dilute, limit where weight fraction $Cr_2O_3 \ll 1$, proportional to the Cr_2O_3 weight fraction. For the latter calculation, the width at half peak intensity of the Cr_2O_3 (104) line was used (15).

Table 3 shows the relative intensity I_r and crystallite size d (Å) obtained on the α-Al_2O_3-supported catalysts. The results indicate that heat treatment leads to an increase in both the intensity and average crystallite size of crystalline Cr_2O_3. The 13% Cr-γ alumina catalyst showed no lines due to Cr_2O_3 in agreement with the results of other investigators (7). It must also be pointed out that we saw no displacement of X-ray diffraction lines indicative of the formation of α-solid solutions of Cr_2O_3–Al_2O_3, even in the heat-treated catalysts.

DISCUSSION

The early studies by O'Reilly and Mac-Iver (16) and Eischens and Selwood (17) of chromia–alumina systems provide a basis for the interpretation of our results. The former established the existence, via EPR measurements, of different phases of chromia in chromia–alumina systems: primarily a highly dispersed δ phase consisting of isolated Cr^{3+} ions, and a β phase consisting of clumped or aggregated Cr^{3+} ions

resembling $\alpha\text{-}Cr_2O_3$. While the δ phase was shown to predominate at low Cr loadings, higher loadings led to increasing contributions from the β phase. Similarly the earlier magnetic susceptibility studies of Eichens and Selwood showed that for impregnated chromia–alumina catalysts, as the chromium content increased, clumps of chromia are formed on the alumina surface. Investigating the effect of using different types of alumina, they reported that chromia supported on $\alpha\text{-}Al_2O_3$ formed aggregates that were much more massive than those formed on high area supports. Yao and Bettman (18) and Yu-Yao and Kummer (6) have also used arguments based on different phases to explain oxidation activity of a variety of supported base metal oxide catalysts. We will employ O'Reilly and MacIver's terminology of phases in a more qualified manner and designate as β phase the chromia entities which exhibited X-ray diffraction lines characteristic of crystalline Cr_2O_3, and as δ phase the entities that do not exhibit such lines.

It is clear that all our catalysts contain Cr in excess of monolayer requirements which, for our support, can be calculated as 0.45% Cr (5). Thus, it is likely that the deposition of Cr on the support resulted in a nonuniform buildup of material containing δ and β phase-like entities. The β phase character increased with Cr loading (as shown by the intensity of diffraction lines) in keeping with the results obtained by others (16, 17). Heat treatment led to both an increase in intensity as well as significant Ostwald ripening of the β phase (Table 3). Moreover, the 1% Cr catalyst, which did not exhibit X-ray diffraction lines prior to heat treatment, underwent phase transformation and possibly redistribution of material as manifest by the appearance of diffraction lines, upon heat treatment. Significantly all catalysts that prior to heat treatment displayed higher activity also exhibited β phase character.

TABLE 4

Variations in Catalyst Activity with Cr Loading

Catalyst	Rate[a] in dry air at 523° K	m[b], Nominal order of $r \times n$ in O_2 pressure at 523° K	I_r/d (Å)[c] $\times 10^4$
1.0% Cr	0.0055	+0.37	0.0
1.86% Cr	0.0422	+0.14	0.8
3.38% Cr	0.0703	−0.16	2.3
5.21% Cr	0.0618	−0.11	1.6
13.0% Cr on γ-alumina	0.0412	—	—
1.0% Cr heat treated	0.0422	—	0.6
1.86% Cr heat treated	0.0377	—	0.4
3.38% Cr heat treated	0.0542	—	0.8
5.21% Cr heat treated	0.0552	—	1.6

[a] ml CO_2(STP)/g·cat-min, rate normalized to 1% CO, calculated from least square derived Arrhenius constants.

[b] Obtained from rate in O_2 at 523 K.

[c] Derived from Table 3.

Furthermore the activity of the 1% Cr catalyst, marginally superior to the support activity prior to heat treatment, becomes comparable with the activity of the higher Cr loading catalysts after heat treatment, i.e., after the β phase becomes manifest. It would thus appear that superior CO oxidation activity is associated with the β phase crystalline Cr_2O_3. Reaction rates at 523 K which do not correlate linearly with either wt% Cr or the relative intensity I_r of crystalline Cr_2O_3 do however show a monotone relationship with I_r/d (Å) as seen from Table 4. The fact that the latter quantity is, under reasonable assumptions, proportional to the surface area of the β phase may be construed as further support for the view that the β phase Cr_2O_3 is in large measure responsible for the activity of these catalysts in CO oxidation. The increasing contribution of crystalline Cr_2O_3 to catalyst activity may also be inferred from the shifting of reaction orders in O_2 pressure with increasing Cr loading from positive to negative (Table 4), the latter being characteristic of bulk Cr_2O_3.

While a correlation between activity and β phase character appears to be clear, the gas adsorption results are less conclusive since the relative extent and contribution of each phase to the overall uptake is not known. The relatively high temperatures at which these measurements were made makes it difficult to interpret these in terms of chromia surface area. Table 2 shows that all catalysts adsorb substantial quantities of O_2 and heat treatment causes a further increase in such uptakes. Since a comparison of O_2 uptakes reported on a highly dispersed chromia (δ type) and bulk Cr_2O_3 (5, 14) indicates that the former adsorbs significantly more O_2, it would seem reasonable to expect that the X-ray invisible δ phase contributes significantly to total O_2 uptake. Quantitative conclusions are precluded due to the multiphase nature of the chromia.

Yu Yao and Kummer (6) studied the effects of heat treatment on several forms of base metal oxide (CuO, CO_3O_4, NiO, and $CuCr_2O_4$) catalysts. Mechanical mixtures of active metal oxide with supports increased their activity 10 to 200-fold when heat treated while impregnated catalysts showed the same or slightly diminished activity. Except for the 1% Cr our catalysts appeared to conform to this behavior. They interpreted the increased activity of their mixture catalysts as due to the spreading out, on heat treatment, of the active metal oxide to form a large area δ phase. Even allowing for some similar and necessarily much more limited spreading or "establishment" of a δ phase on heat treatment, the evidence would seem to indicate that the δ phase of α-Al_2O_3-supported chromia possesses small activity compared to the β phase and that the increase in 1% Cr activity is almost entirely due to the formation of a significant, well-defined, β phase.

A comparison of the activity of our impregnated α-Al_2O_3 supported catalysts with data on other forms of chromia catalysts is

in order here. If one allows the extrapolation of rate data to a temperature of 573 K, a point about 25 K outside the studied range, calculation using the Arrhenius constants of the 3.38% Cr non-heat-treated catalyst predicts a rate of 0.7 ml CO_2(STP)/ g·cat-min. At the same temperature and for a similar H_2O free 1% CO concentration, the specific rate reported on bulk Cr_2O_3 (1) is 0.03 ml CO_2(STP)/m^2-min, which, even if one divides the rate on the impregnated catalyst by the entire support area, shows it to have a specific activity about five times that of the bulk Cr_2O_3, and orders of magnitude higher than that of γ-alumina-supported chromia (5). Thus the enhancement of activity hoped for together with the thermal stability needed seems in fact to be achievable on the α-Al_2O_3-supported catalysts, perhaps through the formation of β phase Cr_2O_3 entities that cannot be attained on other types of support. However, similar to the results obtained in hydrocarbon oxidation over bulk Cr_2O_3 (4), our data (Figs. 2, 4) indicate that H_2O inhibition of CO oxidation is severe at the temperatures we employed, and that this susceptibility is not significantly influenced by changes in the activating procedures for catalysts.

REFERENCES

1. Kummer, J. T., "Catalysts for the Control of Automotive Pollutants." ACS Advances in Chemistry Series No. 143, 1975.
2. Yu Yao, Y. F., J. Catal. 39, 104 (1975).
3. Hertl, W., and Farrauto, R. J., J. Catal. 29, 352 (1973).
4. Yu Yao, Y. F., J. Catal. 28, 139 (1973).
5. Bridges, J. M., MacIver, D. S., and Tobin, H. H., Actes 2nd Congr. Intern. Catalyse, Paris, 1960. Editions Technip, Paris, 1961.
6. Yu Yao, Y. F., and Kummer, J. T., J. Catal. 46, 388 (1977).