JOURNAL OF CATALYSIS **102**, 172–179 (1986)

Comparative Study of Alumina-Supported CuO and $CuCr_2O_4$ as Catalysts for CO Oxidation

FRANCISCO SEVERINO, JOAQUÍN BRITO, OSWALDO CARÍAS, AND JORGE LAINE[1]

Laboratorio de Catálisis Heterogénea, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela

Received June 14, 1985; revised November 26, 1985

Alumina-supported CuO and $CuCr_2O_4$ catalysts of various compositions were prepared and their activity for CO oxidation measured. Fresh, pretreated with CO, and reoxidized catalysts were studied. In general, the activity increased with the CO pretreatment. The extent of the activation depended on the catalyst composition. Thus, copper catalysts were more active than copper chromite at low metal concentrations (<12 wt%), but the opposite was observed at concentrations higher than about 12 wt%. The results on activity behavior, together with TPR and XRD spectra, suggest that the active species are related to copper cations. In the low concentration copper catalysts, the most active surface is generated after CO pretreatment, followed by a fast reoxidation occurring at the first stages of the reaction. In the high concentration copper catalysts, the CO pretreatment produced an induction period as a result of excessive reduction. It is suggested that the role of chromium is to limit the extent of reduction through the formation of the $CuCr_2O_4$ phase. The presence of this phase also resulted in catalysts less prone to deactivation, as compared to copper on alumina catalysts.

INTRODUCTION

A few decades ago, carbon monoxide oxidation could be defined as a classical reaction of basic catalysis research (*1, 2*). However, governmental regulations have now focused attention on this reaction in the automobile-emission control field, causing the latter to be worldwide the largest market for catalyst application.

One of the most effective nonprecious metal catalysts for CO oxidation seems to be the copper–chromium combination (*3, 4*). However, the information regarding Cu–Cr oxidation catalysts is not comprehensive and there is no clear definition of the role of each metal as well as of the influence of the support. Thus, for example, either chromium (*5, 6*) or copper (*7, 8*) has been considered to be the main active species. Also, the studies have been carried out employing different pretreatment conditions, namely either reducing (*5, 9*) or oxidizing (*6, 10, 11*) atmospheres, which could produce different results.

The concentration of the most efficient catalyst has been reported in the patent literature to be around 5 to 20 wt% on alumina, with a metal composition close to Cr/Cu = 1 rather than Cr/Cu = 2 (*12*), which corresponds to the stable form of copper chromite, $CuCr_2O_4$. However, there is not a clear interpretation for this optimal concentration and composition.

The structure of alumina-supported copper catalysts has been extensively studied and several phases have been identified (*13–19*), but few works have been devoted to the possible relations between the catalyst structure and its activity for carbon monoxide oxidation. In addition, there are some contradictions about the nature of the Cu-active sites in the monometallic supported catalyst. For example, Cu/Cu_2O interface or nonstoichiometric Cu_2O or Cu phase (*13*), dispersed copper (*14*), and six-coordinated copper(II) species (*15*) have been proposed as active species.

---

[1] To whom correspondence should be addressed.

0021-9517/86 $3.00

In this work we present an attempt to relate the activity with the structure of copper- and copper–chromium-supported catalysts of various compositions and submitted to various pretreatments, with the aim in probing the role of each of the constituents of the mixed catalyst.

EXPERIMENTAL

The catalysts were prepared by impregnating γ-Al_2O_3 (BDH, 150 mesh, 95 m^2/g) with an aqueous solution of copper and chromium nitrates. After evaporating the excess solution at 60°C, the paste obtained was dried at 100°C and calcined by increasing the temperature at a rate of 100°C/h until 500°C, at which temperature it was kept overnight. Three series of catalysts were prepared: CuO/Al_2O_3, $CuCr_2O_4/Al_2O_3$, and Cr_2O_3/Al_2O_3 with metal concentrations ranging between 2 and 30%. The series of chromia catalysts did not present any detectable activity under the experimental conditions employed in this work (see below); therefore, we report results concerning only the Cu and Cu–Cr catalysts.

The catalyst activities at 200°C were measured in a flow system previously described in detail (*20*). The reactant atmosphere was a mixture of 30 ml/min of CO (99.5%, used as received) plus 150 ml/min of air (dried over drierite and molecular sieves). The amounts of sample were chosen in order to have a constant Cu + Cr weight of 10 mg. These were diluted with the alumina support to have a catalyst bed of 2 g.

Catalytic activity was determined for fresh, prereduced, and reoxidized catalysts. In a typical experiment, a fresh sample of catalyst was placed in the reactor and temperature was set at 200°C under a flow of helium before introducing the reactant mixture. Prereduction was carried out with undiluted CO (30 ml/min) at 300°C for 3 h. The most active catalysts caused an exothermic effect when introducing the reactants together. This gave rise to a temporary increase of the temperature above the set value of 200°C. Reoxidation was performed after prereduction with CO by passing a flow of air for 3 min before mixing with CO for reaction. The exothermic effect cited above was significantly diminished by this procedure.

Temperature-programmed reduction (TPR) of the catalysts was carried out as described elsewhere (*21*). Briefly, the apparatus consisted of a flow system connected to a thermal conductivity cell to follow changes in the composition of the reducing gas (10 ml/min of CO plus 40 ml/min He). The reactor was a Pyrex tube (12 mm diameter) with an internal frit to hold the catalyst sample. This consisted of sufficient catalyst to provide 25 mg of Cu, diluted with pure alumina to 100 mg. Alumina itself did not have any TPR signal in the working conditions. The reactor was positioned in a tubular furnace which was heated at a constant rate (20°C/min) from 50 to 500°C. CO_2 formed in the oxidation was removed by means of a liquid nitrogen trap at the outlet of the reactor. Thus, the observed signal was related only to CO consumption.

X-Ray diffraction (XRD) spectra were carried out using Cu$K\alpha$ radiation, Ni filter, and 40 kV. Samples for XRD were removed from the reactor after CO treatment or reoxidation under an inert atmosphere at room temperature and taken immediately for XRD measurement. More experimental details are given below.

RESULTS

Color changes. Table 1 shows the catalyst colors resulting from changes in the atmosphere of treatment. These colors were found to be more variable in the case of low concentration Cu catalyst.

The sample with 2% Cu presented the following changes: when the CO pretreated sample (black) was left open to the laboratory conditions (70% relative moisture) it returned gradually to its original color (clear blue) after approximately 48 h. However, this change did not occur when kept in an inert atmosphere. It was also observed

TABLE 1

Characteristics of Fresh Catalysts and Changes in Color after Pretreatments

Catalyst	Metal composition (wt %)	BET surface area (m²/g)	Color		
			Fresh	Reduced[a]	Reoxidized[b]
CuO/Al_2O_3	2	90	Clear blue	Black	Clear gray
	5	85	Green–blue	Black	Gray–brown
	10	75	Gray	Red–black	Gray–brown
	20	65	Gray	Red	Dark red
	30	50	Dark gray	Red	Dark red
$CuCr_2O_4/Al_2O_3$	2	85	Yellow mustard	Dark gray	Gray–green
	5	80	Clear brown	Black	Dark green
	10	70	Dark brown	Black	Gray–black
	20	65	Black	Black	Black
	30	55	Black	Black	Black

[a] Reduction with CO at 300°C.

[b] Reoxidation with dried air at 200°C.

that when the 2% Cu sample was reoxidized with dried air, its gray tone was kept even at the laboratory atmosphere.

Catalyst activities. The steady state activities of the catalyst after the different pretreatments are shown in Fig. 1. In the absence of CO pretreatment, the Cu catalysts were more active than the Cu–Cr catalysts for all concentrations. In general, CO pretreatment increased the steady state activity of all catalysts. The increase in activity was more pronounced for the very low (2%) concentration Cu sample and for high concentration Cu–Cr samples. This response to CO pretreatment produced two optimum metal concentrations, which are about 5% for the Cu series and about 20% for the Cu–Cr series. It can also be observed that the CO pretreatment made the Cu–Cr catalyst more active than the Cu catalysts at concentrations above 12%. The activities of samples reoxidized in both series of catalysts were similar to those corresponding to nonreoxidized-CO-pretreated samples; however, the Cu series presented more noticeable differences.

Figures 2 and 3 show the behavior of the catalytic activity with the time exposed to the CO/air stream, after different pretreatments. In the case of the sample with 2% Cu, an exothermic effect increased the reactor temperature temporarily above the

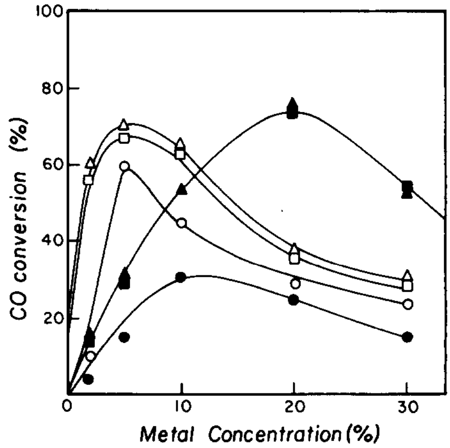

FIG. 1. Steady state activity of copper and copper chromite catalysts after different pretreatments. Reaction temperature: 200°C. Sample: 10 mg of supported metals. Open symbols, CuO/Al_2O_3; filled symbols, Cu Cr_2O_4/Al_2O_3. Catalyst pretreatment: (○,●) fresh, (▽,▼) CO reduced, (□,■) reoxidized.

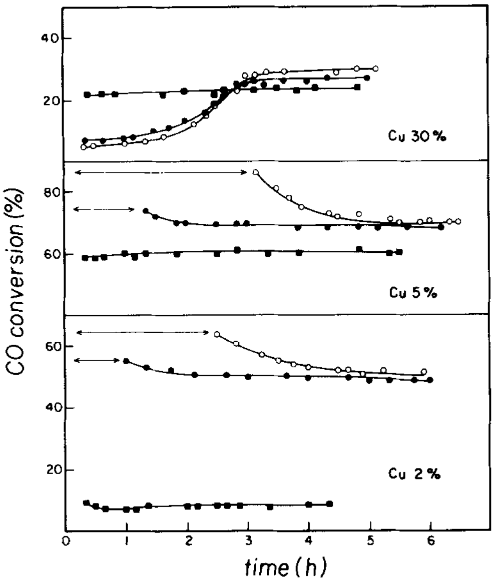

FIG. 2. Activity behavior at 200°C of some CuO/Al$_2$O$_3$ catalysts. Pretreatment: (■) fresh (a), (○) reduced (a + b), (●) reoxidized (a + b + c). Note: initial period of time without data (denoted by (←→) was due to temperature elevation by the exothermic reaction.

set value (200°C). After the temperature was stabilized at 200°C a progressive deactivation was observed in the sample pretreated with CO. When the same catalyst was reoxidized (pretreatment: a + b + c) both the exothermic effect and deactivation were less pronounced. Similar behavior occurred with the 5% Cu sample.

In the case of the sample with 30% Cu, there were no exothermic effects. Both samples, that pretreated with CO and the reoxidized, presented induction periods of activation after which the activity increased to values near to that of the unpretreated sample.

The exothermic effect was also observed in the Cu–Cr series (Fig. 3) and it was approximately proportional to the steady state activity. However, there were neither pronounced deactivations nor induction periods as observed in the Cu series.

XRD spectra. Figure 4 shows the XRD spectra for the Cu catalysts. The presence of metallic copper can be seen in the CO-pretreated samples, even at the lowest Cu concentration where the CuO phase could not be detected in the fresh catalyst.

The spectrum of 30% Cu reduced catalyst was little affected by reoxidation suggesting that oxidation of bulk metallic copper is more difficult than oxidation of dispersed metallic copper.

Figure 5 shows the XRD spectra for the Cu–Cr catalysts, where both crystalline CuCr$_2$O$_4$ and Cr$_2$O$_3$ are present. It also can be seen that small peaks of metallic copper appeared after the CO pretreatment. These results suggest that all the copper in the Cu–Cr catalyst is not forming the CuCr$_2$O$_4$ phase; therefore, some of the Cu nondetectable by XRD might be interacting with the support, probably as CuAl$_2$O$_4$.

Figure 6 shows the variation of the relative intensity of the Cu peak at $2\theta = 43.4°$ after CO pretreatment. The amount of metallic copper remarkably increases with Cu concentration in the nonchromium series. However, the mixed Cu–Cr catalyst series have a constant amount of metallic copper, approximately equal to the amount found in the low concentration Cu catalysts. This

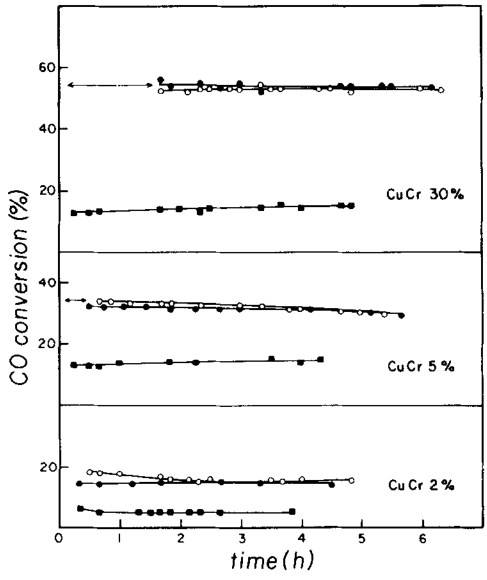

FIG. 3. Activity behavior at 200°C of some CuCr$_2$O$_4$/Al$_2$O$_3$ catalysts. Pretreatment and note: as in Fig. 2.

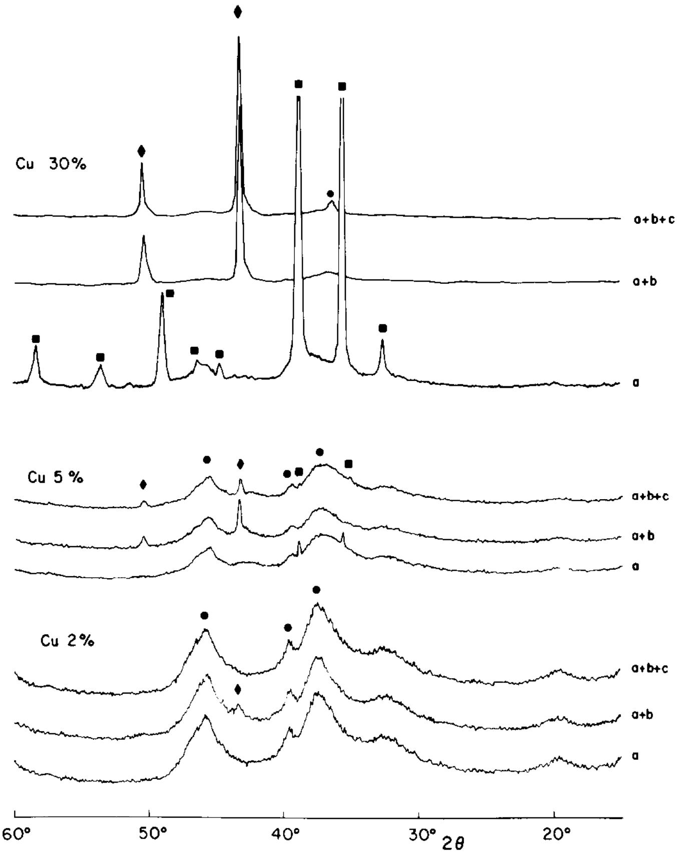

FIG. 4. XRD spectra of some CuO/Al_2O_3 catalysts, after different pretreatments: a, fresh oxide; b, pretreated with CO; c, reoxidized. Phases: (●) γ-Al_2O_3, (■) CuO, (◆) Cu.

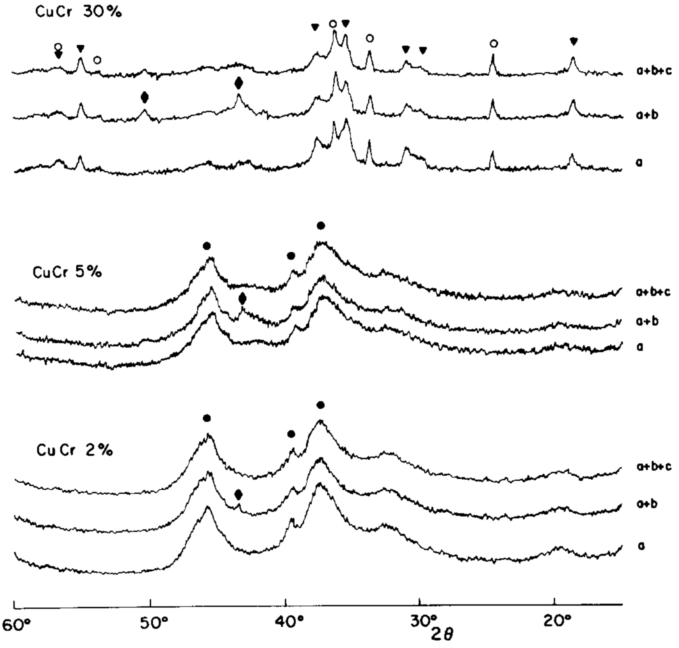

FIG. 5. XRD spectra of $CuCr_2O_4$/Al_2O_3 catalysts after different pretreatments: a, b, and c as in Fig. 5. (●) γ-Al_2O_3, (◆) Cu, (▼) $CuCr_2O_4$, (O) Cr_2O_3.

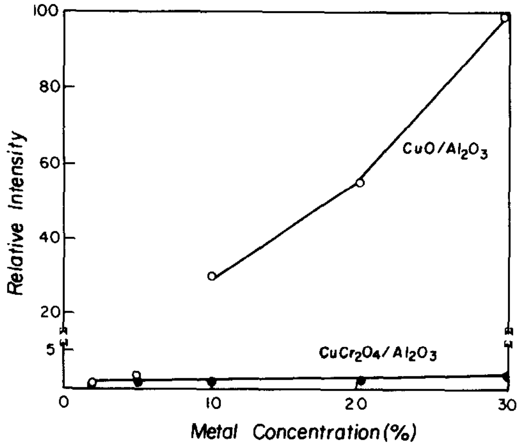

FIG. 6. Variation of the relative intensity of Cu peak at $2\theta = 43.4°$ after CO pretreatment. (○) Copper catalysts, (●) copper chromite catalysts.

suggests that copper associated with the alumina support is reduced more easily than copper associated with chromia. Besides, the almost constant concentration of metallic copper may be assigned to a constant surface saturation value of CuAl$_2$O$_4$.

TPR spectra. Figure 7 shows the temperature-programmed reduction patterns of samples weighted to constant Cu content. It is seen that chromium significantly affects the copper reducibility. The CuO catalysts were more reduced when the metal concentration increased, while the presence of copper chromite caused catalyst reducibility to decrease with increase of metal concentration.

The first peak that appears in the Cu–Cr samples in Fig. 7 has an intensity which almost remains constant with metal concentration up to about 20%. Therefore, this peak could be attributed to CuAl$_2$O$_4$ which has been suggested above to have a constant concentration (Fig. 6). The second peak can be assigned to CuCr$_2$O$_4$ which is more difficult to reduce as its concentration increases, contrary to what has been observed for CuO. It should be emphasized that the two parameters which give a measure of the catalyst reducibilities, i.e., the integral area under the TPR curve and the peak temperature, confirm that the catalyst is protected by Cr against reduction.

The broken lines depicted in the TPR spectra of Cu samples indicate the possibility of a peak tail instead of a second broad peak, i.e., there is a negative signal over the tail that may correspond to desorption of CO reversibly adsorbed (*22*). As long as the tail signal does not return to the baseline, the possibility of CO consumption by a reaction such as 2CO → C + CO$_2$ has to be taken into account for further investigation.

DISCUSSION

Previous works (*3, 8*) have reported that CuCr$_2$O$_4$ is more active than CuO for CO oxidation; however, it is seen from Fig. 1 that this is the case only if prereduction is carried out and if the concentration on the alumina support is larger than about 12%.

The induction period observed after prereducing the high concentration Cu cata-

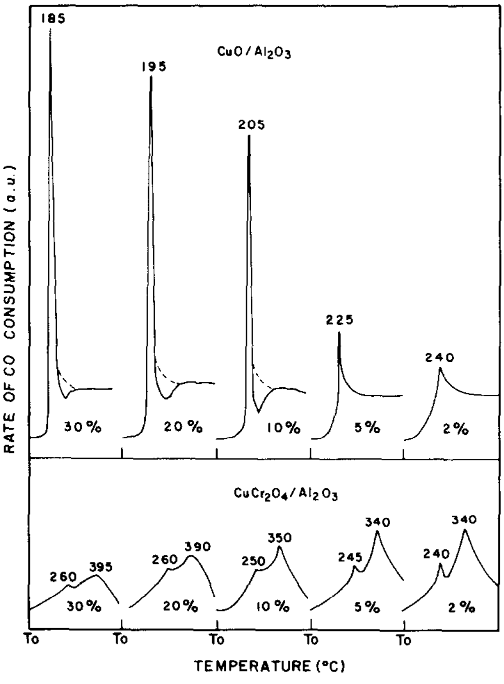

FIG. 7. TPR spectra. Rate, 20°C/min; range, 50 ($=T_0$) – 500°C. Weight of copper was constant in all samples. CO consumption of supported Cr$_2$O$_3$ was almost undetectable.

lysts (Fig. 2) was probably due to excessive reduction to metallic copper, as suggested by XRD (Fig. 4). This means that copper reoxidation is not easy under the experimental conditions employed.

At low concentrations (less than about 12%), and with CO prereduction, Cu catalysts were more active than Cu–Cr catalysts (Fig. 1). At these low concentrations, it should be expected that some significant fraction of the copper is forming the surface aluminate $CuAl_2O_4$. This was suggested by the above XRD and TPR results and has also been found in a previous work (*17*) where a saturation of the alumina support with a surface aluminate was reported at a concentration of about 4% for each 100 m^2/g of alumina surface for a calcination of 500°C. This concentration is close to the optimum found for the Cu catalysts (Fig. 1). Reduction of this phase should produce a metallic copper dispersion, as suggested by the appearance of small and broad XRD signals of metallic Cu (Fig. 4). Also, it showed the characteristic black color (Table 1) which has been reported (*23*) for the copper dispersion on alumina. Therefore, the activity of the low concentration Cu catalysts is due to well-dispersed copper cations exposed at the surface of the alumina, which, contrary to the bulk CuO, are easily formed in the oxidation atmosphere of the reaction. This latter suggestion was confirmed by both the decrease of metallic Cu-signal after reoxidation (Fig. 4) and the absence of induction periods in the low concentration Cu catalysts (Fig. 2).

In the case of high concentration (e.g., 20%) Cu–Cr catalysts, it should be expected that most of the copper is available at the precursor surface as $CuCr_2O_4$ rather than $CuAl_2O_4$. Accordingly, the activity should be attributed in this case to $CuCr_2O_4$ crystallites as detected by XRD, and the decrease in activity observed after about 20% of metal concentration is merely a consequence of surface area decrease (Table 1) by dilution of the support.

In low concentration Cu–Cr catalysts, chromium probably does not enter the alumina lattice by calcination as easily as copper does, but rather stays on the surface forming a Cr^{5+} dispersion (*24*), bidimensional clusters, and small crystallites of Cr_2O_3 (*25*). There is some evidence of formation of Cr_2O_3–Al_2O_3 solid solutions. However, this seems to happen only when both oxides are prepared by coprecipitation (*26*). Accordingly, in the low concentration catalysts inactive chromia can cover the surface copper cations linked to the alumina lattice, suppressing the capability of CO adsorption on Cu sites, which results in lower catalytic activity (Figs. 1 and 3).

Comparing the most active Cu and Cu–Cr catalyst activities, i.e., 2–5% Cu (Fig. 2) and 20–30% Cu–Cr (Fig. 3), it can be seen that Cu catalysts are affected by pronounced deactivation whereas the CuCr catalysts are not. Thus, it can be speculated that active copper sites in $CuCr_2O_4$ are less prone to deactivation, i.e., are more stable, than active copper on alumina. However, the deactivation observed seems to be occurring by a process caused by oxidation, as reoxidation (a + b + c pretreatment) produced a catalyst with activity similar to the steady state activity of the CO-pretreated catalyst (Fig. 2). Nevertheless, we cannot establish a clear interpretation for the deactivation from the present results, without further evidence regarding changes of Cu dispersion after the pretreatments and after reaction.

From the TPR and XRD spectra, the following order can be established for reduction:

$$CuO > \text{surface } CuAl_2O_3 > CuCr_2O_4 > Cr_2O_3 > Al_2O_3$$

It may be interesting to remark that both $CuCr_2O_4$ and $CuAl_2O_4$ compounds are spinel types (*27*), indicating that the divalent cation (Cu) is stabilized by the spinel structure. Furthermore, stabilization is more effective in $CuCr_2O_4$ than in $CuAl_2O_4$, as the latter is more easy to reduce and more prone to deactivation as discussed above. The $CuCr_2O_4$ structure is a normal spinel, i.e., most copper cations are in tetrahedral sites (*27*, *28*), with only a small inversion, less than 10% (*29*). In contrast, $CuAl_2O_4$ is a partially inverse spinel with 40% copper at octahedral sites, but inversion can reach values up to 80% when the aluminate is well dispersed at the surface (*17*). Therefore, it can be concluded that copper cations are stabilized in tetrahedral sites more than in octahedral sites.

The above discussion suggests that chromium is a promoter which inhibits excessive reduction of copper in the high concentration catalysts. The role of CO pretreatment in the mixed catalyst seems to be to create a larger number of oxygen vacancies which could not be effectively generated by the reactant atmosphere, which may be considered oxidizing in nature.

As a result of a certain amount of copper forming part of the aluminate, and hence not being available at the surface in high concentration Cu–Cr, it should be anticipated that the best Cr/Cu value is not the same as that corresponding to the stoichiometry of $CuCr_2O_4$, but corresponding to a smaller Cr/Cu value, probably tending to the stoichiometry of $Cu_2Cr_2O_4$. This has been reported in the patent literature (*12*), the optimum catalyst concentration corresponding to a value of Cr/Cu between the two above.

ACKNOWLEDGMENTS

The authors thank the Venezuelan Gran Mariscal de Ayacucho Foundation and the Consejo Nacional de Investigaciones Científicas y Tecnológicas (Grant CONICIT S1-1184) for financial assistance. Special thanks to Ms. S. Bencosme for her comments.

REFERENCES

1. Stone, F. S., "Advances in Catalysis," Vol. 13, p. 1. Academic Press, New York, 1962.
2. Katz, M., "Advances in Catalysis," Vol. 5, p. 177. Academic Press, New York, 1953.
3. Shelef, M., Otto, K., and Gandhi, H., *J. Catal.* **12,** 361 (1968).
4. Yu Yao, Y. F., and Kummer, J. T., *J. Catal.* **46,** 388 (1977).
5. Lory, E. C., *J. Phys. Chem.* **37,** 685 (1933).
6. Farrauto, R. J., and Hertl, W., *J. Catal.* **29,** 352 (1973).
7. Yur'eva, T. M., Boreskov, G. K., and Gruver, V. Sh., *Kinet. Katal.* **10,** 294 (1969).
8. Roth, J. F., and Doerr, R. C., *Ind. Eng. Chem.* **53,** 293 (1961).
9. Frazer, J. C. W., and Albert, C. G., *J. Phys. Chem.* **40,** 101 (1936).
10. Morgan, W. L., and Farrauto, R. J., *J. Catal.* **31,** 140 (1973).
11. Kingsbury, P. I., and Hertl, W., *J. Catal.* **32,** 333 (1974).
12. Farrauto, R. J., Hoekstra, K. E., and Shoup, R. D., U.S. Patent 3,870,658 (1975).
13. Pierron, E. D., Rashkin, J. A., and Roth, J. F., *J. Catal.* **9,** 38 (1967).
14. Mooi, J., and Selwood, P. W., *J. Amer. Chem. Soc.* **74,** 2461 (1952).
15. Summers, J. C., and Klimisch, R. L., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 293. North Holland/American Elsevier, Amsterdam/New York, 1973.
16. Lo Jacono, M., and Schiavello, M., *in* "Preparation of Catalysts" (B. Delmon, P. A. Jacobs, and G. Poncelet, Eds.), p. 473. Elsevier, Amsterdam, 1976.
17. Friedman, R. M., Freeman, J. J., and Lytle, F. W., *J. Catal.* **55,** 10 (1978).
18. Sventsitskii, E. S., Vorob'ev, V. N., and Talipov, G. Sh., *Kinet. Katal.* **18,** 201 (1977).
19. Ertl, G., Hierl, R., Knözinger, H., Thiele, N., and Urbach, H. P., *Appl. Surf. Sci.* **5,** 49 (1980).
20. Severino, F., and Laine, J., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 396 (1983).
21. Brito, J., and Laine, J., *Polyhedron,* **5,** 179 (1986).
22. Hall, W. K., *in* "Proceedings, 4th Conf. on The Uses and Chemistry of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 224. Climax Co., Ann Arbor, Michigan, 1982.
23. Wolberg, A., and Roth, J. F., *J. Catal.* **15,** 250 (1969).
24. Jagannathan, K., Srinivasan, A., and Rao, C. N. R., *J. Catal.* **69,** 418 (1981).
25. Poole, C. P., and MacIver, D. S., "Advances in Catalysis," Vol. 17, p. 223. Academic Press, New York, 1967.
26. Eischens, R. P., and Selwood, P. W., *J. Amer. Chem. Soc.* **69,** 1590 (1947).
27. Wells, A. F., "Structural Inorganic Chemistry," 3rd ed., pp. 457, 487. Oxford Univ. Press, London, 1962.
28. Wyckoff, R. W. G., "Crystal Structures," 2nd ed., Vol. 3. Interscience, New York, 1965.
29. d'Huysser, A., Wrobel, G., and Bonnelle, J. P., *Nouv. J. Chim.* **6,** 437 (1982).