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Copper Oxide on Alumina

I. XRD Studies of Catalyst Composition during Air Oxidation of Carbon Monoxide

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In situ X-ray diffraction and differential thermal analysis have been applied to a study of a supported oxide catalyst used in the air oxidation of CO to CO_2. Studies have been made of a given catalyst that has been activated to several different metastable states. The X-ray studies under reaction conditions reveal pronounced differences in composition for the variously activated catalysts. Activation involves reduction to Cu_2O and Cu, and the formation of lattice heterogeneities. The active sites of the metastable catalysts studied are associated with the interface between Cu^{1+} and Cu^0 phases, and/or nonstoichiometric Cu_2O and Cu phases. The X-ray results under reaction conditions differ from these obtained at ambient conditions.

INTRODUCTION

It is well known that metal oxides, supported or unsupported, can undergo transformation when they are used as oxidation catalysts. Usually it has been difficult to establish the nature of these transformations. The technique of *in situ* X-ray diffraction (XRD) analysis, recently reported for a bismuth molybdate catalyst (*1*), can be used to make direct observations of the crystalline phases of a catalyst under reaction conditions. This technique has now been applied to a study of copper oxide supported on alumina during the catalytic oxidation of carbon monoxide by air.

It has previously been observed in kinetics studies (*2*) that a composite consisting initially of cupric oxide dispersed on alumina could be activated by various treatments so that it exhibited a variety of metastable states. It was presumed that each of the different activated states of the catalyst reflected some change in composition. The present study was undertaken, therefore, to determine whether *in situ* XRD studies could be used to uncover information on the nature of the activation process, and, possibly, of the active sites. Some differential thermal analyses (DTA) have been performed to help establish phase transformations in the system: copper oxide on alumina.

EXPERIMENTAL

The DTA and XRD apparatus and sample handling procedures have been described previously (*1, 3*) Two gas sample tanks were used for the *in situ* XRD studies: one contained a reaction mixture of carbon monoxide and air similar in composition to that used in the kinetics studies—75.4% nitrogen, 19.7% oxygen, 4.8% carbon monoxide (mole % analysis determined by gas chromatography); the other tank contained Matheson CP grade carbon monoxide and was used for catalyst reduction.

Catalyst activity data were obtained in a fixed-bed stainless steel tubular reactor of 1-inch internal diameter using catalyst

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beds of 5.0-ml volume. The reactor was heated by means of electrical heater bands with temperature being controlled to a maximum variance of ±0.1°C. Flow was controlled precisely with flow controllers and measured with capillary flow meters. In general activity data on a given catalyst was reproducible to within ±2%. The standard condition used for determining activity employed a total flow rate of 8500 cc/min and a reaction temperature of 135°C. Extent of conversion of CO to CO_2 was determined by gas chromatography using a silica gel column and thermistor detectors. In the case of those highly activated catalysts which gave CO to CO_2 conversions greater than a few mole percent, there was a pronounced exotherm and the nominal reaction temperature of 135°C was substantially exceeded. Nevertheless, the fact of exceptional activity was clearly indicated.

The catalyst was prepared by impregnating a commercial gamma alumina (Harshaw 0104 1/8 × 1/8-inch cylindrical tablets) with a hot solution of reagent grade $Cu(NO_3)_2 \cdot 3H_2O$. Sufficient solution was used to just completely saturate the pellets, and the impregnate was vigorously stirred to assure a uniform preparation. The composite was then dried for 20 hr at 120°C and calcined in air at 500°C for 12 hr. The copper content (as Cu) was determined by chemical analysis to be 10.5 wt %.

From the kinetics studies it was determined that at least three different catalyst pretreatments before the standard activity run at 135°C produced a more active catalyst than no pretreatment at all. The three pretreatments were also performed on the catalyst during the *in situ* XRD runs to determine the structures they produced and to relate these to the higher activity. The three pretreatments are as follows:

(a) The catalyst was heated in the reaction mixture (4.8% CO in air) for 1 hr at 270°C.

(b) The catalyst was heated in pure CO for 1 hr at 175°C.

(c) The catalyst was heated at 250°C, exposed to pure CO for 15 min, then exposed to air for 15 min, and was subjected to three such cycles.

After each pretreatment was finished, the catalyst temperature was lowered to the reaction temperature (135°C) in the pretreatment atmosphere and then, the reaction mixture was turned on and allowed to flow through the XRD cell. The catalyst was subjected to reaction conditions for a specified period of time before starting the XRD run.

In addition to making structure studies after pretreatments under reaction conditions, "conventional" structure studies were also performed after the pretreatments. For the "conventional" structure determinations, the following procedure was followed: After each pretreatment, the catalyst was allowed to cool down to room temperature with the pretreatment atmosphere flowing through the cell. When the catalyst reached room temperature the pretreatment atmosphere was turned off and air turned on. The sample was allowed to purge in air for 15 min before starting the XRD run. For the pretreatment involving the three cycles of reduction-oxidation, the last step of the third cycle already had air flowing through the cell so in this case the air flow was continued during the cool-down to room temperature and then the air was allowed to purge for an additional 15 min before starting the XRD run.

RESULTS AND DISCUSSION

A. DTA and XRD Study in Air of Supported Copper Oxide

The DTA thermogram for the catalyst calcined at 500°C revealed two regions of thermal activity: (1) a weak and broad endotherm peaking near 100°C very similar in appearance to the 100°C endotherm observed for the bare support, and (2) a weak and broad exotherm between 1000° and 1100°C, peaking near 1050°C. The region of the thermogram between 125° and 1000°C was flat. The thermogram for the dried catalyst (120°C) exhibited a sharp endotherm of medium intensity between 200° and 300°C peaking near 260°C. This peak represents the endothermal decomposition of $Cu(NO_3)_2$ to CuO. The thermogram for the pure support showed no thermal activity except for the weak endotherm peaking near 100°C.

A thermogram was also obtained for pure CuO [prepared by heating $Cu(NO_3)_2 \cdot 3H_2O$ in air at 500°C for 12 hr]. The thermogram was flat from room temperature to 1000°C. Between 1000° and 1100°C a strong and broad endotherm was observed, peaking near 1075°C. This is likely due to decomposition of CuO to Cu_2O. This strong high-temperature endotherm was also observed in the thermograms for pure $Cu(NO_3)_2 \cdot 3H_2O$ and pure $CuSO_4$. On running a cooling curve the transformation was, in all cases, reversible. This transformation seems to be characteristic of pure CuO for it was not observed in the supported catalyst. As noted earlier, a weak unidentified exotherm between 1000° and 1100°C was observed for the supported catalyst, indicating some other process involving CuO and Al_2O_3.

The results obtained for elevated temperature *in situ* XRD studies in air of the supported catalyst are summarized in Table 1. XRD study of the pure support from 24° to 900°C revealed only γ alumina. For each determination in Table 1 the cell was continuously flushed with air (30 ml/min) and the sample was maintained at each temperature for 45 min before starting the XRD run. The first observance of α-Al_2O_3 occurs at 700°C with the transformation being nearly complete at 800°C. The complete disappearance of γ-Al_2O_3 occurs at 900°C. The observed temperature of 700°C for the formation of α-Al_2O_3 is much lower than the literature value of 1100°C (4, 5). A possible explanation for the lower temperature is the presence of the spinel structure, $CuAl_2O_4$, which first appears at 700°C and which apparently catalyzes the formation of α-Al_2O_3 at a lower temperature. Other workers (*6, 7*) have reported the formation of the spinel $CuAl_2O_4$ at 800°C from a study of coprecipitated hydroxides (Lowell) and CuO–Al_2O_3 mixtures (Misra).

TABLE 1

STRUCTURE OF SUPPORTED CATALYST CALCINED IN AIR AT 500°C

Temperature (°C)	Height of major peak (mm)			
	γ-Al_2O	CuO	$CuAl_2O_3$	α-Al_2O_3
25°	30	110	0	0
500°	30	110	0	0
600°	30	95	0	0
700°	10	40	52	10
800°	5	5	115	85
900°	0	0	120	90
1000°	0	0	120	90

As noted earlier the thermogram for the catalyst showed no thermal activity in the region of 700°C where we know from the XRD studies that the CuO and Al_2O_3 are reacting to form the spinel compound. Thermochemical calculations made by Gadalla and White (*8*) on the reaction of CuO and Al_2O_3 to form the spinel show that the heat of reaction is not zero. Thus it appears that the explanation of negative DTA results around 700°C lies in a very slow rate of spinel formation. This explanation reveals a limitation in the DTA technique and emphasizes the importance of using other physical techniques along with DTA to get an accurate and complete picture of thermal behavior.

B. XRD Studies of Supported CuO Under Reaction Conditions

Data from the *in situ* XRD studies performed under reaction conditions and in the "conventional" way are given in Tables 2–6. The results are listed in chronological order of various treatments. The times (min) appearing in all the tables were determined by measuring the time between the start of the particular atmosphere and temperature conditions and when the goniometer moved to $2\,\theta = 35°$ (this is roughly 15 min after the start of the XRD run).

In all cases, the rate of gas flow through the XRD cell was maintained at 30 ml/min. To minimize time delays in reaching atmosphere equilibrium in the 350-cc XRD cell, and to permit the sample surface to be immediately in contact with the incoming atmosphere, the end of the gas inlet tube in the cell was bent so that the gas flow

TABLE 2

Supported CuO; Pretreatment: None

Temperature (°C)	Atmosphere	Time (min)	Catalyst composition: Height of major XRD peak, in mm CuO	Cu_2O	Cu
25°	Air	120	150	0	0
135°	Air	35	150	0	0
135°	4.8% CO in air	35	148	0	0
135°	4.8% CO in air	120	147	0	0
135°	Air	100	148	0	0
25°	Air	35	149	0	0

impinged directly on the sample. Studies using 5, 10, 20, and 30 ml/min gave nearly identical results and indicate that the precautions taken above were adequate to assure atmosphere equilibrium. These studies involved repetitive duplications of a given pretreatment and demonstrated the high reproducibility of the XRD results shown in Tables 2–6. Six sets of quadruplicate activations reproduced the XRD peak heights with an average deviation of 1–2 mm. Hence most of the differences appearing in Tables 2–6 are judged to be significant.

Separate detailed studies using a gas flow of 30 ml/min were made of the alumina support and pure unsupported CuO. The support under both reaction and nonreaction conditions for times ranging from 25 min to 120 min shows no changes. The XRD patterns reveal only γ-alumina.

A similar degree of inertness is observed for the most part with unsupported pure CuO. For all the various conditions studied, including a 75-min exposure at 270°C in 4.8% CO in air, one observes the presence of only CuO with no changes occurring in sample composition. However, on exposing the sample to pure CO at 270°C for 75 min complete reduction of CuO to metallic copper occurs. This inertness exhibited by pure CuO on exposure to the reaction atmosphere at 270°C is to be contrasted with the behavior of supported CuO under similar conditions. From line 1 of Table 3 it is seen that after a similar exposure the supported CuO has been reduced to both Cu_2O and copper. This demonstrates the greater reactivity of the oxide when highly dispersed on the surface of a support.

Table 4 shows the results for the three cycle pretreatment. This pretreatment was studied in greater detail by examining the composition of the catalyst during the separate reduction and oxidation periods of each cycle with some interesting findings: after only 5 min of the reduction period of the first cycle the supported CuO had undergone complete reduction to metallic copper. Further, the reduction of CuO to Cu seems to be direct for no Cu_2O was observed during the reduction period. During the air oxidation period of the first cycle the continuous oxidation of metallic copper to Cu_2O is observed. At the end of each of the three cycles one does not observe the reappearance of CuO in the sample. Under the conditions studied it is not possible to reoxidize the copper back to CuO.

The catalyst compositions (Tables 3–5) are different under reaction conditions than at usual ambient conditions. The last two results in Table 5 show clearly that a change in composition occurs when the catalyst is simply exposed to air at 25°C.

Table 6 summarizes the results for catalyst compositions arising from each of the three pretreatments, and the corresponding activity data. The more active compositions all contain significant amounts of reduced CuO. Even the sample having no pretreatment could have its low level of activity associated with reduced phases whose amounts are simply too small to be detected by XRD. This could be up to 5–10% of the total copper present, assuming 0.5–1.0 wt % of crystalline material as the limit of detection by XRD.

The most active compositions are those containing appreciable amounts of both Cu_2O and Cu. This suggests the possibility that activity depends on the coexistence of Cu_2O and Cu phases, and that the active sites may be found at the interface of these phases. In the case of carbon monoxide oxidation over cobalt oxide supported on alumina, it has been proposed by Tomlinson and co-workers (*9*) that enhanced activity may occur at active sites located

TABLE 3

SUPPORTED CuO; PRETREATMENT: 1 HR AT 270°C IN 4.8% CO IN AIR

			Catalyst composition			
			Height of major XRD peak, in mm			
Temperature (°C)	Atmosphere	Time (min)	CuO	Cu_2O	Cu	Cu_2O/Cu
135°	4.8% CO in air	45	146	45	10	4.5
135°	Air	45	155	3	6	0.5
25°	Air	45	155	3	6	0.5
25°[a]	Air	30	155	4	9	0.44

[a] Conventional structure study performed after pretreatment.

TABLE 4

SUPPORTED CuO; PRETREATMENT:
CO FOR 15 MIN FOLLOWED BY AIR FOR 15 MIN AT 250°C—THREE CYCLES

			Catalyst composition			
			Height of major XRD peak, in mm			
Temperature (°C)	Atmosphere	Time (min)	CuO	Cu_2O	Cu	Cu_2O/Cu
135°	4.8% CO in air	20	0	105	25	4.2
135°	4.8% CO in air	45	0	105	25	4.2
135°	Air	45	0	105	25	4.2
25°	4.8% CO in air	45	0	105	25	4.2
25°[a]	Air	30	0	120	18	6.67

[a] Conventional structure study performed after treatment.

TABLE 5

SUPPORTED CuO; PRETREATMENT: 1 HR AT 175°C IN PURE CO

			Catalyst composition			
			Height of major XRD peak, in mm			
Temperature (°C)	Atmosphere	Time (min)	CuO	Cu_2O	Cu	Cu_2O/Cu
135°	4.8% CO in air	45	0	20	160	0.12
25°	4.8% CO in air	45	0	20	160	0.12
135°	Air	45	0	22	155	0.14
175°[a]	CO	45	0	0	200	0
25°[b]	Air	30	0	6	180	0.03

[a] Performed 45 min after start of pretreatment.

[b] Conventional structure study performed after pretreatment.

TABLE 6

SUMMARY OF STRUCTURE AND ACTIVITY DATA FOR SUPPORTED CuO

	Catalyst composition (reaction conditions)					
	Height of major XRD peak, in mm					
				Cu_2O/Cu		
Pretreatment	CuO	Cu_2O	Cu	R.C.[b]	Conven.[c]	Activity[a] (%)
4.8% CO in air, 1 hr 270°C	146	45	10	4.5	0.44	50
CO and air at 250°C, three cycles	0	105	25	4.2	6.67	57
CO for 1 hr at 175°C	0	20	160	0.12	0.03	0.60
None	147	0	0	0	0	0.36

[a] Mole % conversion of CO to CO_2 at one standard set of reaction conditions.

[b] R.C., reaction conditions.

[c] Conven., conventional structure study.

at the interface between Co^{2+} and Co^{3+} phases. These workers invoked this suggestion to explain an observed minimum in activation energy in the Co/Al_2O_3 system.

The proposal that the active sites in the copper system are related to the crystalline phases is supported by the relation between activity and total copper content. At low copper concentrations, it has been found (*10*) that there is a marked decline in specific catalytic activity for carbon monoxide oxidation. Magnetic susceptibility (*10*) and ESR (*11*) studies have shown that dispersion increases as copper content is lowered, and this is accompanied by the disappearance of crystallinity.

Table 7 shows the results of line shape analysis of the XRD peaks obtained during the cyclic pretreatment. As the number of reduction and oxidation treatments increase, the heights of the Cu and Cu_2O peaks decrease slightly (the height after the third cycle being 85% that after the first cycle). In contrast, the peak width at half-height doubles. This effect is observed after the reduction as well as oxidation cycles. These results indicate that the cyclic treatment produces a significant amount of lattice heterogeneities in both the Cu and Cu_2O crystal phases. The Cu_2O phase so produced may be analogous to the metastable nonstoichiometric copper oxide, $CuO_{0.67}$, found by Wieder and Czanderna (*12*) in their studies of the oxidation of thin copper films and described by them as a gross defect structure of Cu_2O. In any case, the activation accompanying the cyclic treatments leads to the formation of disordered Cu_2O and Cu phases and the possible generation of active sites in one or both of these phases.

TABLE 7
LINE SHAPE ANALYSIS OF XRD PEAKS DURING THE CYCLIC PRETREATMENT

Pretreatment condition	Width of Cu peak at 1/2 the height, in mm (Analytical peak, d = 2.09 Å)
After 1st CO reduction	5
After 2nd CO reduction	7
After 3rd CO reduction	10
	Width of Cu_2O peak at 1/2 the height, in mm (Analytical peak, d = 2.14 Å)
After 1st oxidation	6
After 2nd oxidation	7
After 3rd oxidation	13

CONCLUSIONS

From the known relation between specific catalytic activity and copper content, it is concluded that the active sites for carbon monoxide oxidation over copper oxide supported on alumina are associated with the bulk (at least partially crystalline) phases of copper oxide. *In situ* XRD studies have shown that the activation of cupric oxide on alumina involves the generation of reduced copper phases (Cu_2O and Cu) and the formation of lattice heterogeneties. It seems unlikely that the phase CuO, per se, participates in the catalysis. It appears that the active sites are associated with (1) the interface between Cu_2O and Cu phase and/or (2) nonstoichiometric Cu_2O or Cu phase. The present results do not permit one to distinguish between these possibilities. It is important to note that these conclusions apply to catalysis in the temperature regime of 100° to approximately 160°C where metastable states exist. At significantly higher temperatures, the catalysis may very well involve alternate oxidation reduction of the copper oxide phases and proceed via an entirely different mechanism than that operative under the conditions of the present investigation.

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