Poisoning by SO$_x$ of Some Base Metal Oxide Auto Exhaust Catalysts

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Many base metal oxide catalysts used for carbon monoxide and hydrocarbon oxidation in automobile exhaust gas are poisoned by sulfur oxides. A study was made of SO$_x$ interaction with several catalysts (copper chromite, copper oxide, cobalt oxide, and commercial copper chromite containing copper oxide) to determine its effect on catalytic activity. Various techniques were used in concert and included infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry as a measure of catalytic activity, and chemical analysis. The catalytic activity was determined as a function of the amount of SO$_2$ adsorption at various temperatures, and the specific surface sites were identified.

The results indicated that there are at least two different adsorption sites for SO$_2$ on copper chromite; the SO$_2$ adsorbs preferentially on the site most important for CO oxidation; the sites necessary for hydrocarbon oxidation being less affected. No sulfate ions form on stoichiometric copper chromite, in contrast to the other catalysts studied.

The extent of regeneration of poisoned catalysts depends on the catalyst composition, and several regeneration methods are discussed.

INTRODUCTION

Copper chromite can be prepared to resist the high temperatures expected (~800°C) in an automobile exhaust and for this reason has been considered a candidate for controlling emissions. However, the catalytic performance deteriorates in an atmosphere containing sulfur oxides. Several studies of SO$_x$ poisoning of base metal oxidation catalysts have been reported (*1–4*). The interaction of SO$_2$ with specific active sites of a copper chromite catalyst has also been investigated (*5*).

This paper presents the results of a study of the adsorption and desorption of sulfur oxides by copper chromite, and the effect that this has on oxidation catalysis of hexane and carbon monoxide (the former being somewhat representative of unburned hydrocarbon).

Thermogravimetry was used to examine the details of the interaction of SO$_x$ with the catalyst and differential scanning calorimetry to test relative catalytic activity. Detailed studies of different SO$_x$ poisoning mechanisms of several base–metal catalysts (CuO, Co$_3$O$_4$, and CuO + CuCr$_2$O$_4$) using chemical analysis and surface infrared spectroscopy are also discussed.

EXPERIMENTAL

Catalyst Preparations

A thermally stable copper chromite catalyst can be prepared by removing any excess CuO by a hydrochloric acid leach. We have found that this gives a material that shows no further chemical or physical changes when heated at temperatures not exceeding 800°C. It is prepared by mixing aqueous solutions of Cu(NO$_3$)$_2$·3H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O with a final concentration of 2 M with respect to each cation. The solution is dried at 110°C and the nitrates

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decomposed at 200°C. The oxides are then fired to 600°C for 4 hr. X-ray diffraction results show two phases: CuO and $CuCr_2O_4$. If this mixture is heated to 800°C, a chemical reaction producing some $Cu_2Cr_2O_4$ occurs. Formation of this undesired product can be prevented if the oxide mixture is first leached for about 1 hr in $3 M$ HCl, thoroughly washed, and subsequently fired to 800°C. The only phase then present is $CuCr_2O_4$, herein designated L-$CuCr_2O_4$. The surface area as determined by the Brunauer, Emmett, and Teller method using N_2 was consistently 6 m²/g after repeated firings to 800°C for up to 72 hr. Furthermore, the 1500 Å particle size, the X-ray diffraction pattern, and the catalytic activity for carbon monoxide and hydrocarbon oxidation were essentially unchanged. Since the material's properties are stable, we use it for a reference base–metal oxide catalyst.

Cobalt oxide was prepared by decomposing solid cobalt carbonate at 250°C with subsequent firing to 800°C for 16 hr. X-ray diffraction identified only Co_3O_4. The surface area was 4 m²/g.

Copper oxide was prepared by drying an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$, decomposing the nitrate at 200°C and firing to 700°C for 4 hr. The physical surface area of 0.4 m²/g was reduced to almost 0.1 m²/g if the material was fired at temperature higher than 700°C.

Harshaw 1800P copper chromite catalyst was selected for detailed study; the composition has 51% CuO and 47% Cr_2O_3, according to the supplier. After firing for 4 hr to 700°C, x-ray diffraction indicated only CuO and $CuCr_2O_4$ present, and a surface area of 2.3 m²/g. Firing to higher temperatures resulted in formation of $Cu_2Cr_2O_4$.

Preparation of Poisoned Samples

Samples of catalyst powder were held at various controlled temperatures in a flowing gas reactor for 1 hr, after which the cell was purged and rapidly cooled. The synthetic exhaust gas mixture was SO_2: 0.08%, NO: 0.1%, C_3H_6: 0.1%, CO: 1.25%, H_2O: 3%, O_2: 7%, and N_2: balance.

A flow rate of about 2 liter/min was used through about 5 g of catalyst. We chose a high SO_2 level (relative to that usually found in automotive exhaust gas) in order to accelerate the poisoning. Portions of the SO_2-treated catalyst were used for DSC samples, TGA samples, and regeneration studies.

Additional poisoning studies were also performed using 10,000 ppm SO_2 in excess air.

DSC Testing

A duPont Model 900 thermal analyzer with a differential scanning calorimeter (DSC) cell is used to test catalytic activity. A small pan of powdered sample is heated at 20°C/min in a flowing test gas atmosphere, and the temperature rise, ΔT, relative to an inert reference used as a measure of catalytic activity. Details are given elsewhere (6). In a separate experiment, a sample was heated to 500°C, held at that temperature, and the steady-state ΔT displayed on a time-base recorder. Sulfur dioxide (100 ppm) was then added to the test gas, and a record of ΔT versus time was made.

Thermogravimetric Analyses

A Mettler thermoanalyzer was used to obtain TGA data. Both desorption from poisoned samples and reaction of the sample in an atmosphere with SO_x were studied.

The previously treated samples were heated in air at a rate of 10°C/min to 800°C and held at that temperature for up to an additional 3 hr. The weight change versus time was recorded, and normalized to show weight percent change.

Other runs were made using the corrosive gas furnace and show directly the reaction of SO_x with the catalyst. The major constituent of the experimental atmosphere was dry air flowing at 6 liter/hr, with SO_x being introduced through a port in the top of the furnace to produce a mixture having 1000 ppm. The source of SO_2 was a 1.56% blend in N_2, while that for SO_3 was β-sulfur trioxide crystals in a glass tube held at −20°C and purged with N_2 carrier gas.

Two types of runs were made using 100 mg of sample in an alumina crucible. To determine the temperatures where adsorption and desorption occur, the sample was heated to 300°C and cooled to 50°C, then SO_x was introduced and the temperature raised to 800°C at a rate of 10°/min. Adsorption kinetics were studied by heating a fresh sample to 500°C, after which SO_x was added and the weight gain versus time recorded under isothermal conditions.

Chemical Analysis

Chemical analyses for sulfur of poisoned and unpoisoned catalysts before and after water washing were performed using a LECO IR-32 automatic sulfur determinator that employs a high temperature induction combination, followed by measurement of the SO_2 formed using an infrared detector. Soluble cobalt was determined using the NITROSO-R salt method (7) and copper by the BATHOCUPRIONIC method (7).

Infrared Spectroscopy

These studies were conducted as previously reported (5).

RESULTS

Effect of SO_2 Exposure Temperature on Catalytic Performance

The poisoning of L-$CuCr_2O_4$ by sulfur oxides is strongly temperature dependent. Figure 1 shows CO oxidation catalytic activity of samples that had been exposed for 1 hr to ~800 ppm SO_2 in a reactor at several different temperatures. The samples exposed at room temperature and 400°C were severely poisoned. The 700°C sample was only slightly more resistant, and no difference was found between samples heated to 800°C in synthetic exhaust atmospheres, which did or did not contain SO_2. A 24-hr soak at 800°C is sufficient to regenerate catalysts that had been poisoned at lower temperatures. Although the minimum time at 800°C for complete regeneration was not determined, we found that more than 1 hr is required.
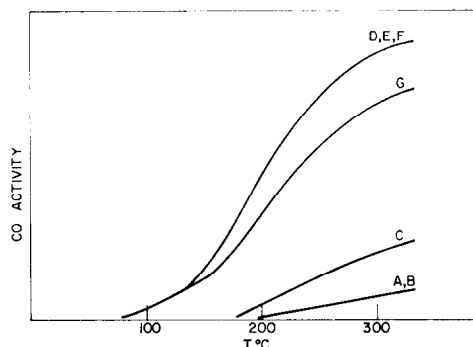

FIG. 1. CO activity as a function of SO_2 poisoning at various temperatures for L-$CuCr_2O_4$. (A) Room temperature exposure 1 hr 800 ppm SO_2. (B) 400°C exposure. (C) 700°C exposure. (D) 800°C exposure. (E) 800°C, 24 hr, no SO_2. (F) A, B, and C, 800°C, 24 hr air. (G) A, B, and D, 800°C, 1 hr, air.

Similar results were found for hexane oxidation activity.

Thermogravimetric analysis results from these poisoned samples are given in Fig. 2. The data have been compensated by subtracting the results from measurement of an untreated sample, and normalized to a weight percent basis. Weight losses at low temperature might not be entirely SO_2, but also may include some H_2O, which was present perhaps in greater abundance in the samples that had been treated in the reactor. Desorption from the sample

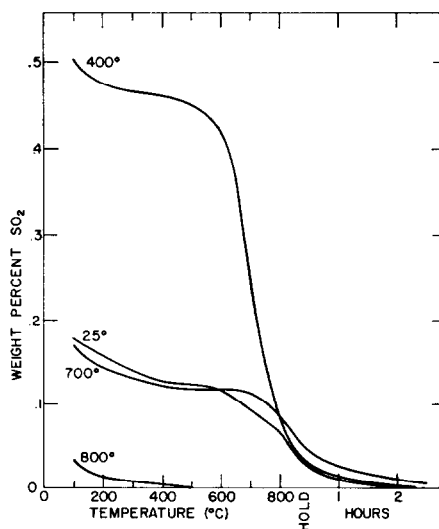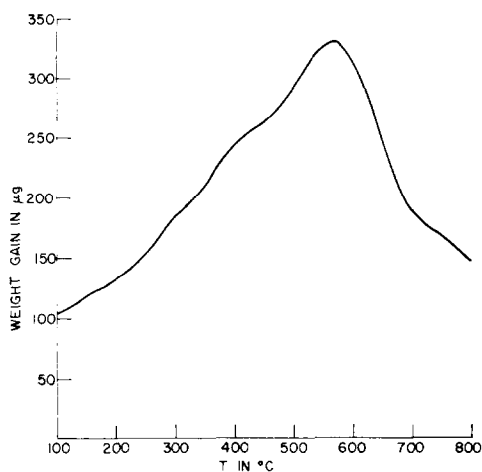FIG. 2. Thermal gravimetric analysis for L-$CuCr_2O_4$ exposed to SO_2 at various temperatures.

FIG. 3. Adsorption of SO_2 on L-$CuCr_2O_4$ as a function of temperature. Heating rate 10°C/min, 1000 ppm SO_2 in air. Sample weight 100 mg.

treated at 700°C took place more slowly than that from samples treated at lower temperatures, suggesting possible differences in bonding mechanisms of the SO_2 on the catalyst surface.

Data showing pickup and loss of SO_2 by fresh catalyst dried at 300°C immediately prior to the run are shown in Fig. 3 as a function of temperature during heating to 800°C at a rate of 10°/min. This is a convenient method for rapid scanning of the use temperature regions for adsorption–desorption. One finds continuous adsorption of SO_2 to about 575°C where desorption begins with about half of the SO_2 remaining when the temperature reaches 800°C. A "base line" from a blank run has been subtracted to compensate changes in air buoyancy during the temperature scan. An alumina crucible was used to hold the sample, since earlier runs in a platinum-rhodium vessel resulted in significant SO_3 formation. Some SO_3 was formed during the runs in alumina, undoubtedly through catalysis by the sample.

SO_2 Isothermal Adsorption

Adsorption kinetics were determined by measuring the weight gain at 500°C versus time after the addition of 1000 ppm SO_2 to the furnace atmosphere. Data are given in Fig. 4. The 500°C temperature was chosen
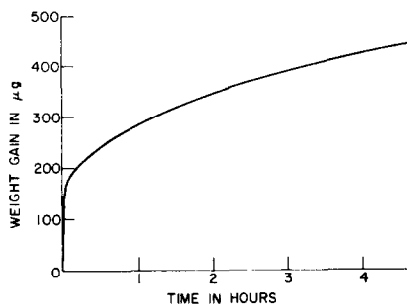

FIG. 4. Isothermal adsorption of SO_2 on L-$CuCr_2O_4$ at 500°C. 1000 ppm SO_2 in air. Sample weight 100 mg.

to represent an average exhaust gas temperature. The adsorption occurs via at least two processes, designated "fast" and "slow," which are at "carbonyl" and "carbonate" sites, respectively (5).

One can separate the processes in the following way. The total weight M that would be picked up by the sample if the measurements had been taken until there was no further weight change is estimated. Then a plot of $\log[(M - m)/M]$ versus time is made, where m is the weight gain at a particular time. Figure 5 shows the result, which has the striking feature of linear behavior within the accuracy of the weight detection system for almost 4 hr of the experiment.

There are not sufficient data to determine reaction kinetics for the fast process, especially since the SO_2 concentration is building up in the reaction chamber during
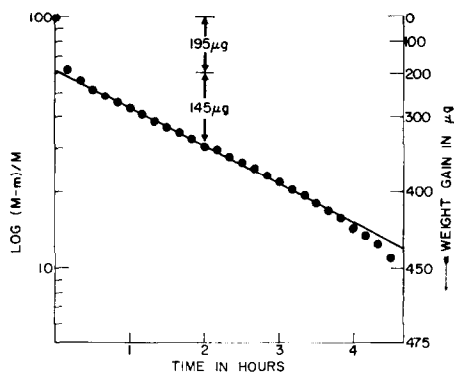

FIG. 5. Analysis of the isothermal adsorption of SO_2 (in air) on L-$CuCr_2O_4$ at 500°C.

the initial stages of the experiment. The slow process (adsorption onto the "carbonate" sites) follows first order kinetics. If we write $M_1 + M_2 = M$, with M_1 the total pickup via the fast process ("Carbonyl" sites) and M_2 that via the slow process, then the rate equation for the latter is

$$\frac{dm}{dt} = K(M_2 - m), \text{ giving}$$

$$\ln[M_2/(M_2 - m)] = Kt.$$

The value of M_1 can be obtained from the $t = 0$ intercept of the straight line, and is 195 μg for the data of Fig. 5. Considering the analogy of the slow process to radioactive decay, we can define a half-time for the coverage. This is found to be $2h$. During the first half-time, one half of the total coverage occurs, giving $M_2 = 290$ μg. This gives $M = 4.85$ mg/g-cat. for this experiment.

Data similar to those in Figs. 4 and 5 were obtained using $\sim$1000 ppm SO_3 in excess air. The curves had the same general shape, with $M_1 = 1.10$ mg/g-cat, $M_2 = 1.40$ mg/g-cat. and $t_{1/2} = 33$ min.

The fast process of Fig. 5 shows an adsorption of 2 mg of SO_2 per gram of catalyst, about 3 mol/100 Å.^{2}

Catalytic Performance and in Situ SO_2 Poisoning

Catalyst poisoning, measured by monitoring DSC activity at 500°C subsequent to the addition of 100 ppm SO_2, is shown in Fig. 6. The decrease in CO oxidation is quite severe as the SO_2 is introduced. The initial poisoning rate is quite rapid with subsequent slower deactivation. The decrease in catalytic performance of L-$CuCr_2O_4$ for hexane oxidation is less severe compared with the CO process, a result consistent with our picture of "fast" and "slow" sites. The hexane run was stopped after 30 min in order to minimize possible damage to the cell by acids formed from SO_x and water produced from the hexane oxidation.
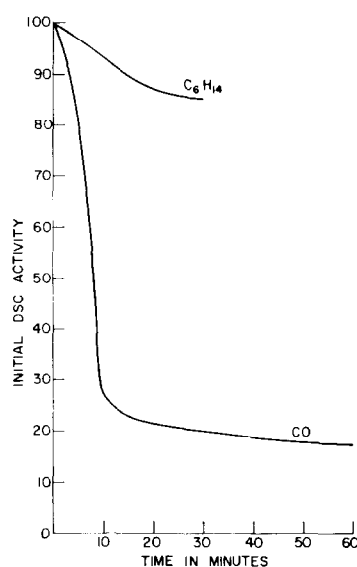
The recovery of CO oxidation at 500°C

FIG. 6. CO and hexane oxidation over L-$CuCr_2O_4$ at 500°C in the presence of 100 ppm SO_2.

after poisoning was also measured. A rapid increase in activity (about 30% in the first 10 min after shutting off the SO_2 supply) followed by slower continued improvement was found. Extent of recovery was not affected by exposure time up to 80 min. After 1 hr, 50% of the activity lost had been recovered, indicating some degree of reversibility in the poisoning of active sites, at least for those sites responsible for CO oxidation at 500°C. Although the experiment was terminated after 1 hr of recovery, there was evidence that the activity was still slowly improving.

Sulfur trioxide was tested and also found to poison L-$CuCr_2O_4$. The adsorption rate at 500°C was similar to that of SO_2. However, the half time of the slow process was only about 30–35 min.

Nature of the Adsorbed Poison

Infrared surface analysis of copper chromite exposed to SO_2 at temperatures up to 400°C gave no evidence of sulfate formation (5). Some bands were found and were assigned to adsorbed SO_2/SO_3, but no $SO_4{}^{2-}$ band at 983 cm^{-1} was present. The experiment has been repeated for L-$CuCr_2O_4$ using 10,000 ppm SO_2 at 500°C,

and only the bands found earlier were present (8).

If the poisoning process of SO_2 involves SO_4^{-2} formation, some of the metal in the catalyst will be water soluble. For samples treated at 500°C in 1000 ppm SO_2, virtually no Cu^{2+} or Cr^{3+} ion was detected in the leachate. The experiments were then repeated at 10,000 ppm SO_2, and 3×10^{-5} mmoles of Cu^{2+} were detected. This is quite close to the blank of 1×10^{-5} mmoles and may not be significant. The total amount of soluble sulfur was 2.3×10^{-4} mmoles, which is approximately four times greater than that adsorbed at 1000 ppm SO_2, cf. Fig. 4. These results suggest the possibility of some SO_4^{2-} formation at higher concentrations of SO_2. However, as mentioned above, infrared was unable to detect its presence. Similar results were obtained when the catalyst was exposed to 10,000 ppm SO_2 at 700°C.

After the catalyst was poisoned at 500°C using either 1000 or 10,000 ppm SO_2 it had lost virtually all of its ability to catalyze CO oxidation below 200°C. After water washing 50%–60% of its original activity was restored. Infrared data substantiated the removal of some bonded SO_2/SO_3, but we are not able to identify the active sites involved. By the extent of regeneration and its importance in the CO oxidation process, it appears likely that it is from the "carbonyl" sites.

Harshaw 1800P was fired to 700°C for 4 hr followed by an HCl leach to remove excess CuO to see if the absence of SO_4^{2-} formation depended on the preparation of the catalyst. This catalyst was exposed to 1000 ppm SO_2 in excess air for 15 min at 500°C. Water leaching and surface infrared failed to show any SO_4^{2-} formation.

OTHER CATALYSTS

Cupric oxide, cobalt oxide and Harshaw 1800P were all tested for poisonability by SO_2. All showed rapid decreases in CO conversion efficiency at 500°C during exposure to 100 ppm SO_2; the curves obtained were similar to those of Fig. 6. After each test, the samples were water leached yielding large quantities of metal ions. The results are in Table 1. In no instance after water washing was more than 20–30% regeneration of original catalytic CO oxidation activity noted.

X-Ray diffraction identified $CoSO_4$ in the Co_3O_4 catalyst and $CuSO_4$ in both the CuO and Harshaw 1800P, the latter originally having substantial amounts of CuO in addition to $CuCr_2O_4$.

Both water leaching and infrared studies of Harshaw copper chromite indicate that it is resistant to sulfate formation below 400°C, unlike the Co_3O_4 and CuO. Furthermore, almost 90% of its original efficiency to catalyze the CO oxidation process was restored after water washing. This was a rather surprising result, since CuO itself forms a sulfate at this temperature (9), and its catalytic activity was not regenerable after water washing. Hence, the "excess" CuO in Harshaw 1800P is chemically and catalytically different than CuO itself.

CONCLUSIONS

Sulfate formation is one mechanism of poisoning by SO_2 for at least three typical transition metal oxide catalysts, CuO, Co_3O_4 and CuO + $CuCr_2O_4$. In the latter sample, the mechanism is temperature dependent with SO_4^{2-} formation occurring above 400°C. Leached copper chromite,

TABLE 1
CHEMICAL ANALYSIS OF SO_2 POISONED CATALYSTS AFTER WATER LEACHING

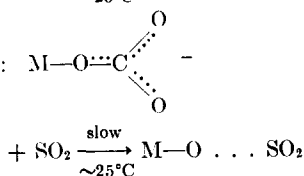|	M^{2+} mg/g	Sol sulfur mg/g	S.A. (m²/g) before poisoning	S.A. (m²/g) after poisoning
Harshaw 1800P	13.5	170.0	2.3	1.0
CuO	9.5	22.7	.4	0
Co_3O_4 (4 m²/g)	24.5	49.1	4.0	1.0
L-$CuCr_2O_4$	2.2	7.2	6.0	6.0

L-$CuCr_2O_4$, interacts with SO_2 via strong chemisorption with no evidence of SO_4^{2-} formation within the temperature interval of 25°–700°C. Furthermore, no poisoning occurs at 800°C in an atmosphere containing 800 ppm SO_2, but this temperature depends on SO_2 concentration as has been shown recently (4).

The selectivity of SO_2 poisoning on the active sites for CO oxidation by copper chromite has been shown, with rapid adsorption onto the "carbonyl" sites and slower adsorption onto "carbonate" sites. The latter sites are also those of hydrocarbon oxidation and are more slowly poisoned than the "carbonyl" sites. The poisoning process on L-$CuCr_2O_4$ may be schematically represented by:

CO oxid. primary sites: $Cu—C≡O$

$$+ SO_2 \xrightarrow[\sim 25°C]{fast} Cu— \ldots SO_2$$
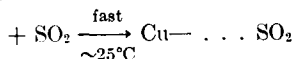
CO oxid. second sites: $M—O≡C\overset{O}{\underset{O}{\diagdown}}$ $^-$

$$+ SO_2 \xrightarrow[\sim 25°C]{slow} M—O \ldots SO_2$$

and H.C. primary sites.

Thermogravimetric analysis showed that at most 3 mol SO_2/100 $Å^2$ adsorb onto the primary active sites for CO oxidation. This is in good agreement with results of Morgan and Farrauto by another method (10).

The mechanism of SO_2 poisoning may be critical in predicting regenerability via water washing. Catalysts via SO_4^{2-} formation show little regenerability, while those samples that poison via SO_2/SO_3 chemisorption (L-$CuCr_2O_4$ and Harshaw CuO + $CuCr_2O_4$ below 400°C) can be regenerated

quite significantly in this way. One can speculate that once SO_4^{-2} is formed and active cations removed by water, the underlying or remaining bulk cations now exposed on the surface are considerably less active. Perhaps this points out differences in the nature of the catalytic surface and original bulk material.

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