JOURNAL OF CATALYSIS 31, 140–142 (1973)

Active Sites on a Copper Chromite Catalyst

INTRODUCTION

Determinations of specific surface area of exposed metal atoms via chemisorption for both unsupported and supported catalysts are commonplace in catalytic research (*1*). This method, although useful, often can not distinguish an adsorption site from a catalytically active site. This problem is even more complex for simple and complex metal oxide systems.

Garner, Stone and Tiley (*2*) have advanced the study of catalytic oxidation of carbon monoxide and the role of adsorbed species on a number of metal oxides, notably Cu_2O. In environments of CO, O_2 and CO–O_2 mixtures, stability of adsorbed species was studied and the catalytically important steps were identified. Inspired by the work of these authors, the present study was undertaken to determine active-site concentration on the surface of a complex metal oxide catalyst. A copper chromite catalyst was selected, since it appears to be an important candidate for control of automobile exhaust pollutants (*3*). Of particular interest in this regard is the temperature at which the catalytic reactor first starts to convert (i.e., lites off). The mechanism for CO oxidation on a copper chromite catalyst has been studied (*4*) and two distinct active sites have been identified. A carbonyl has been found to be active at temperatures in the vicinity of 60–80°C while a less active carbonate species reacts with O_2 to produce CO_2 at approximately 180–200°C. Consequently the carbonyl is responsible for "lites off." The technique described in this paper was developed to measure the number of these carbonyl sites and thus to obtain a better understanding of "lites off."

Some copper chromites were patented in 1936 by Frazer (*5*) for use as exhaust control catalysts for the internal combustion engine. Lory (*6*) in 1933 investigated catalytic behavior of a number of copper chromites while Frazer and Albert (*7*) studied their capacity to adsorb CO and O_2. The latter study was conducted at temperatures in which the bulk of the catalyst is reduced by CO, making adsorption–catalytic relationships doubtful.

The method used in our study was to alternately add O_2 and CO to a copper chromite catalyst at 60°C, which is below its bulk reduction temperature, and monitor the CO_2 produced as a function of each constituent adsorbed. The procedure does not require a knowledge of the mechanism, but information regarding stability of adsorbed species can be obtained (*4*). Furthermore, active-site concentration is determined from the actual catalytic reaction allowing one to differentiate active sites from adsorption sites.

EXPERIMENTAL METHODS

A conventional glass vacuum rack was used for all adsorption experiments. Vacuums of 10^{-5} Torr were routinely obtained using a mercury diffusion pump. Pressures were read on a Wallace and Tiernan gauge.

All gases were prepurified by the Matheson Corp., but were further cleansed of impurities by passing through a liquid nitrogen or molecular sieve (Linde 5A) trap. An additional cold trap was inserted in the outlet manifold to selectively condense only CO_2.

The catalyst was a copper chromite powder prepared by drying an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ which was initially 2 *M* for each metal. After decomposing the nitrates at 250°C, resultant oxides were fired to 600°C for 4 hr. This mixture was composed of only CuO and $CuCr_2O_4$, as determined by X-ray diffraction. The CuO was then removed by an HCl leach (*6*) and the residue was filtered and fired to 800°C for 24 hr. The spinel $CuCr_2O_4$ was identified by X-ray diffraction, and chemical analysis indicated a Cu-to-Cr atomic ratio of 0.53, a slight excess of CuO being in solid solution with the $CuCr_2O_4$ (*8*). The nitrogen surface area was 2.7 m^2/g, as determined by the Brunauer, Emmett and Teller Method.

The catalyst was prepared for adsorption studies by heating to 430°C under an oxygen pressure of 60 Torr for 1 hr. The sample was then evacuated for 16 hr, dosed with 15 Torr of O_2 and cooled to 60°C. Carbon monoxide and O_2 were then alternately added and the CO_2 produced was monitored. The CO pressures were usually about 10 Torr, corresponding to approximately 1.5% in an automobile exhaust, however, experiments up to 45 Torr showed no significant variation in the final equilibrium data. Similar behavior was observed for O_2.

DISCUSSION OF RESULTS

Adsorbed oxygen can be desorbed as CO_2 at 60°C by the addition of CO. Alternatively, O_2 admitted to a copper chromite catalyst with a layer of adsorbed CO also liberates CO_2. The CO_2 can be completely separated from other gaseous constituents by passing through a liquid-nitrogen cold trap. Once the surface is stripped of adsorbed oxygen, further additions of CO result in no detectable CO_2, verifying the absence of bulk catalyst reduction. The amount of CO_2 produced appears to be essentially independent of which gas is adsorbed first. Table 1 gives some typical data of the amount of CO_2 produced during each part of the dosing cycle. The first step is designated as a "cycle break-in," at which time CO is added to the catalyst immediately following the pretreatment. At this time at least two distinctly different types of CO adsorption occur, a strongly chemisorbed species, the carbonate, which can not be removed by either evacuation or oxygen treatment until about 180°C and is unimportant for "lites off" and a second more weakly held entity which can be slowly removed reversibly by evacuation or irreversibly as CO_2 when treated with oxygen. Hence, the first treatment of the surface involves a larger amount of CO adsorption, 0.53 cm^3/g cat., than in subsequent experiments in which 0.25 cm^3/g cat. of CO_2 is produced. Prior to the addition of oxygen the sample tube is evacuated for a short period (less than 5 min) to remove gaseous CO. Some CO is desorbed reversibly during this treatment; however, a residual amount remains, so that dosing with oxygen causes a generation of a definite amount of CO_2, 0.21 cm^3/g cat. By noting the final pressure and amount of CO_2 produced, the extent of oxygen adsorption is found by difference. This procedure was repeated three times. After cycle break-in, each column in Table 1 appears internally consistent. Each dosing results in almost the same amount of CO_2 generation. Hence the amount of CO_2 produced (or O_2 adsorbed) is a measure of the number of active sites for low-temperature catalytic oxidation of CO on $CuCr_2O_4$. The calculations assume that no CO is desorbed reversibly during the oxygen dosing step. In light of the consistent results, this assumption appears justifiable.

TABLE 1
GENERATION OF CO_2 FROM ALTERNATE TREATMENTS OF $CuCr_2O_4$ WITH CO AND O_2

Step	CO (cm^3 ads/ g cat.)	O_2 (cm^3 ads./ g cat.)	CO_2 (cm^3 liberated/ g cat.)
1 (cycle break in)	0.53	—	0.25
2	—	0.105	0.21
3	0.36	—	0.19
4	—	0.085	0.17
5	0.33	—	0.18
6	—	0.085	0.21
7	0.33	—	0.18
8	—	0.085	0.18

Averaging the volume of oxygen adsorbed from Table 1 one obtains 0.085 cm^3/g cat. or 5.10×10^{-18} atoms/g cat. (assuming dissociative chemisorption of oxygen). The BET nitrogen surface area for this catalyst is 2.7 m^2/g cat., so the number of oxygen atoms adsorbed (or available active sites) per 100 $Å^2$ is 1.89.

The SO_2, present in commercial fuels, adsorbs preferentially on these would be active sites seriously retarding "lites off." This was shown in Ref. (*4*) and will be more thoroughly discussed in papers soon to be submitted for publication.

REFERENCES

1. DORLING, T. A., *Dep. Trade Ind.* LR 144 (CA), 1971.

2. GARNER, W. E., STONE, F. S., AND TILEY, P. F., *Proc. Roy. Soc., Ser. A* **211,** 472 (1952).

3. DWYER, F. G., *Catal. Rev.* **6,** 261 (1972).

4. HERTL, W., AND FARRAUTO, R. J., *J. Catal.* **29,** 352 (1973).

5. FRAZER, J. C. W., *U. S. Pat.* 2,031,475, Feb. 18, 1936.

6. LORY, E. C., *J. Phys. Chem.* **37,** 685 (1933).

7. FRAZER, J. C. W., AND ALBERT, C. G., *J. Phys. Chem.* **40,** 101 (1936).

8. GADALLA, A. M. M., AND WHITE, J., *Trans. Brit. Ceram. Soc.* **63,** [10], 548 (1964).

W. L. MORGAN
R. J. FARRAUTO

Corning Glass Works
Research and Development Labs
Sullivan Park
Corning, N. Y. 14830

Received March 19, 1973