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NOTE

Electrical Resistance Changes in Copper Chromite Under Catalytic Conditions

The mechanism and kinetics of CO oxidation over copper chromite have been reported recently (*1*). Of great interest is not only the chemistry of the intermediate adsorbed species, but also the behavior of the catalyst itself under actual catalyzing conditions. To this end, changes in electrical resistance were measured as the atmosphere over the catalyst was changed from O_2 to CO, and from air to an air: 1% CO mixture. The importance of electrical resistance measurements in catalytic studies (*2–4*) lies in the fact that they allow one to obtain a measure of the relative state of oxidation/reduction of the catalyst surface under various conditions. The measurements were paralleled by infrared spectroscopic and vacuum balance experiments carried out under similar conditions.

EXPERIMENTAL METHODS

Resistance measurements were made on a powdered copper chromite catalyst in two sets of apparatus. The first apparatus consisted of a vertical 50-mm glass tube (3-mm i.d.) containing the catalyst and equipped with a centered side-arm for introducing the gases. Close-fitting steel rods were inserted in the ends of the tube for electrical contact and to compress the powder sample. About 1×10^8 dyn/cm^2 was required to make the resistance relatively pressure-independent. Oxygen or carbon monoxide was introduced through the side-arm and forced under pressure through the powder. Venting occurred around the steel rods. In the second apparatus, the powder was distributed loosely between two electrodes at the opposite ends of a 50-mm long transite strip mounted within a 25-mm i.d. glass tube. Air or air + 1% CO was passed over the catalyst powder. Heat was supplied by external heaters in both cases. The resistance of the catalyst powder was measured with a Keithley 610-A electrometer and recorded on a Keithley 370 recorder.

Catalyst weight changes were measured on an Ainsworth recording balance equipped for controlling static atmospheres and temperature. Infrared spectra were made with a Perkin-Elmer 421 spectrophotometer on self-supporting pressed disks which were mounted in a spectrometer furnace connected to a vacuum rack.

Harshaw 1800P copper chromite catalyst was used in all measurements. This material has a surface area of 40 m^2/g and contains cupric oxide (overall molar analysis, 51% CuO and 47% Cr_2O_3).

RESULTS AND DISCUSSION

Spectroscopic studies (*1*) have shown that CO adsorbs on this copper chromite catalyst to form carbonyl groups on exposed copper atoms and unidentate carbonate groups on oxygen atoms. At elevated temperatures both mechanisms lead to reduction of the catalyst. Readily observable quantities of CO_2 appear at about 80°C via the carbonyl mechanism and at about 200°C via decomposition of carbonate groups.

Gravimetric measurements show that, initially, the catalyst gains weight slightly (approx 0.1%) in an atmosphere of 100 Torr CO. At 135°C, this is followed immediately by a continuous weight loss amounting to 0.7% in 1 hr as the catalyst

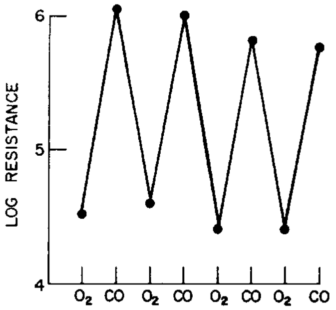

FIG. 1. Resistance changes of copper chromite catalyst as atmosphere is alternated between oxygen and carbon monoxide.

is reduced. Weight losses near 5% were observed in 1 hr at temperatures in the 200–250°C range. These results indicate that oxygen is removed from the bulk of the catalyst since losses of this magnitude are far in excess of the available surface oxygen. On evacuating and then admitting air to the system at the reaction temperature, a rapid increase in weight occurs as the reduced catalyst is reoxidized. Heating to 400°C in air substantially restores the original weight.

In making resistance measurements, no attempt was made to determine the volume resistivity of the catalyst powder due to the confusion introduced by intergranular contact resistance and because of the difficulty in distinguishing between bulk and surface resistivity when the surface-to-volume ratio is large. The purpose of the measurements was to determine the sign of the resistance change as the catalyst was exposed to different atmospheres. The effect of atmosphere on the resistance of the catalyst is large, thus making resistance changes sensitive indicators of relative oxidation state. Figure 1 shows more than an order of magnitude change in the resistance of the catalyst as the atmosphere was alternated between pure oxygen and pure CO at 150°C. Copper oxides display *p*-type conductivity, and the resistance increase during reduction by CO indicates that this catalyst also is a *p*-type semiconductor. The *p*-type conductivity probably results from cation vacancies in the fully oxidized catalyst (*5*). The important point is that reduction of the fully oxidized catalyst causes its resistance to rise, and vice versa.

Figure 2 shows a plot of resistance (solid line) vs time when copper chromite is reduced in CO at 150°C for 10 hr. The resistance first rises but then drops momentarily due to heating associated with the exothermic reaction. After this initial transient, reduction causes the resistance to rise for about 30 min, and then to fall with continued reduction. This decrease can be interpreted in terms of either metallic surface conduction, or the formation of an *n*-type surface region which results from an

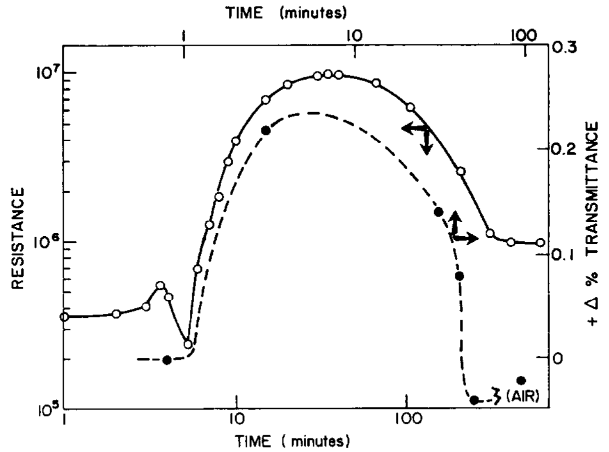

FIG. 2. Time dependence of resistance (○) and transmittance (●) of copper chromite catalyst exposed to carbon monoxide.

excess cation concentration. A large negative temperature coefficient of resistance suggests that the latter interpretation is correct. The resistance of the strongly reduced catalyst increases when it is exposed to oxygen. This behavior would be expected from both models.

Infrared spectra can also be used to monitor resistance changes qualitatively (*6*). The background transmission of any substance, aside from specific absorption bands, will be a function of the carrier density, transmission being inversely proportional to the number of carriers (as is resistance). Thus, we should expect a correlation between background transmission and resistance. When the copper chromite was exposed to pure CO and then evacuated, it was observed that the background transmission did indeed increase. Changes in the percentage background transmission are plotted in Fig. 2 (broken line) for a copper chromite sample standing in an atmosphere of pure CO at 160°C. Allowing for time scale differences due to the different temperatures in the two experiments, it is seen that the changes in background transmission closely parallel the changes in resistance. Since ir spectroscopy is widely used in the study of catalyst surfaces, it is seen that this technique yields the same type of information obtained from electrical resistance measurements.

Figure 3 shows the catalyst resistance changes during the actual catalytic oxidation of CO to CO_2, using 1% CO in air at 250°C. The admixed CO was turned off periodically, allowing only air to flow over the catalyst in order to note the extent to which the resistance changes are reversible. The data show that the catalyst operates in a slightly reduced state, as indicated by the resistance rise, demonstrating that the material goes through an oxidation/reduction cycle when functioning as a catalyst.

The addition of several percent CO to air over a fully oxidized sample at 250°C led to a weight gain of 0.02%, indicating that during catalysis the weight gain due to the formation of the steady-state concentration of chemisorbed surface groups is greater than the weight loss due to oxygen removal. This, together with the moderate resistance rise observed when the catalytic reaction is taking place (Fig. 3), indicates that reoxidation of the catalyst surface is not the rate determining step of the reaction in this temperature region.

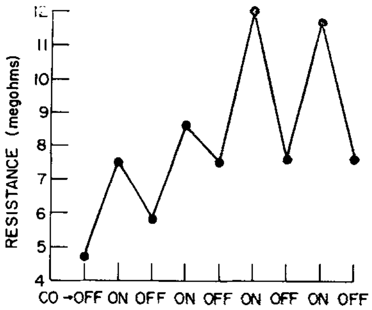

FIG. 3. Resistance changes of copper chromite catalyst for intermittent additions of 1% CO to air.

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