

Section 3

STUDIES OF SURFACE SULFIDATION AND DISTRIBUTION OF SULFUR BY CHEMICAL TITRATION MEASUREMENTS OF SURFACE AREA

3.1 Introduction

The low-pressure process catalysts used in our study were composed of mixed oxides of copper, zinc, and aluminum. During activation by reduction in hydrogen, however, the copper oxide was converted to metallic copper, as determined by x-ray diffraction. Thus, zinc oxide and copper are the active phases for methanol synthesis. To evaluate the individual rates of sulfur coverage of each of these phases during catalyst exposure to sulfur-containing gas, we have measured separately on a single catalyst sample the changes in the respective surface areas of copper and zinc oxide. Our measuring technique is described below.

3.2 Experimental Details

Zinc oxide surface areas have been measured by CO_2 adsorption,^{1*} and copper surface areas, by quantitative measurement of the nitrogen formed by exposure to nitrous oxide.² We have applied these methods to a catalyst containing zinc oxide and copper, since nitrous oxide adsorption on zinc oxide occurs to less than 0.01 monolayer surface coverage,³ and carbon dioxide adsorption on copper is negligibly small.


For our experiments, we used a pulse microreactor system in which a pulse valve was used to inject constant-volume aliquots of either

* References for Section 3 are listed on page 3.4.

nitrous oxide or carbon dioxide into the helium feedstream to a reactor. The reactor, containing about 15 mg of powdered catalyst on a glass frit, was located in the helium carrier stream so that the effluent passed through a gas chromatograph where the components were separated and measured quantitatively. For nitrous oxide decomposition, the gases measured were residual nitrous oxide and nitrogen formed by chemical reaction on the copper surface: $N_2O(g) + Cu \rightarrow N_2(g) + O(s)$ (where g and s refer to gaseous and surface species, respectively). For carbon dioxide, the quantity of residual gas was measured. Thus, the amounts of carbon dioxide lost by adsorption on the zinc oxide and of nitrogen produced by surface reaction on the copper at 300 K represented measures of zinc oxide and copper surface areas, respectively. For poisoning studies, the reactor was switched by a multiport valve out of the helium carrier stream and into a stream of synthesis gas containing 5 ppm hydrogen sulfide in He. After a specified exposure time at 573 K, the reactor was switched back into the carrier stream, reduced in temperature to 300 K, and subsequently pulsed with CO_2 and N_2O to determine changes in the surface areas resulting from hydrogen sulfide exposure.

3.3 Experimental Results

To evaluate absolute surface areas from gas adsorption measurements, we must know to what degree the adsorbate covers the solid at saturation. To avoid uncertainties associated with assigning such values, we report surface areas in terms of percentages of CO_2 adsorbed and of N_2 produced on a freshly reduced catalyst sample of specified mass and particle size. The results of a blank experiment, in which a catalyst sample was aged at reaction temperature in nearly sulfur-free synthesis gas, are presented in Table 3-1. The relative change in surface areas after the catalyst samples are exposed to synthesis gas containing 5 ppm



hydrogen sulfide were corrected for the changes produced by aging. The surface areas were found to decrease exponentially with increasing exposure time to the sulfur-contaminated gas (Figure 3-1). From the slopes of the resulting curves, we conclude that the rate of decrease in the surface area of the copper component is nearly 1.5 times greater than that of zinc oxide.

3.4 Discussion

Aging and sulfur poisoning of the CCI C79-1 catalyst result in significant surface area changes. During aging at reaction temperature in synthesis gas, the zinc oxide surface area was observed to decrease rapidly to a nearly constant value, whereas the copper area showed a steady increase for the duration of our experiment (Table 3-1). Most likely, the increase in copper surface area is due to continued reduction of copper oxide in the highly reducing synthesis gas environment.

Catalytic activity is normally proportional to the surface area of the active components in a catalyst. Consequently, when the catalyst is exposed to hydrogen sulfide-containing synthesis gas, we should expect the surface area decrease to parallel the decrease in methanol synthesis activity. Our model predicts and our poisoning rate measurements have confirmed that methanol yield decays exponentially with hydrogen sulfide exposure. As shown in Figure 3-1, the surface areas of both active components of the C79-1 catalyst exhibit an exponential decay with increasing hydrogen sulfide exposure.

It is difficult to relate the loss in surface area of the catalyst due to sulfur-poisoning, as measured at 1 atm in an integral flow reactor, to the decrease in the rate methanol synthesis determined in a Berty reactor at 500 or 1000 spi. The poisoning coefficient derived from the data in Figure 3-1 is considerably greater than that evaluated from the synthesis results described in Section 1. In part, this difference

may be attributed to the physical makeup of the catalyst bed. For the surface-area studies, a finely powdered catalyst was used, for the synthesis studies at high pressures, the catalyst was in pelletized form. Obviously, any pore-diffusion limitation was greatly reduced and the number of surface-exposed sites was considerably increased for the powdered catalyst sample. The surface area poisoning studies were designed to compare the loss of copper sites relative to zinc oxide with progressive exposure to H₂S.

3.5 References

1. T. Morimoto and K. Morishige, Bull. Chem. Soc. Japan, 47, 92 (1974).
2. T. J. Osinga, B. G. Linsen, and W. P. Van Beek, J. Catalysis, 7, 277 (1967).
3. J. Cunningham, J. J. Kelly, and A. L. Penny, J. Phys. Chem., 74, 1992 (1970).

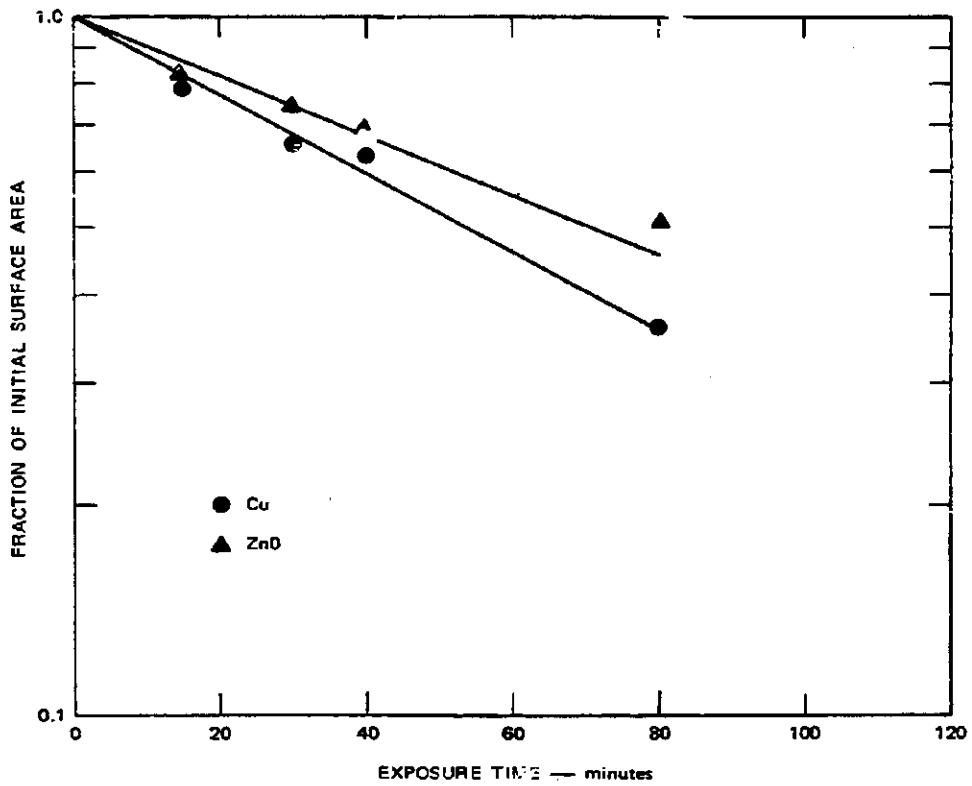
Table 3-1

CHANGES IN SURFACES AREAS OF C79-1 CATALYST
EXPOSED TO SYNTHESIS GAS AT 573 K

Total Exposure to Synthesis Gas ^a	Percent of Initial ZnO Area (by CO ₂ adsorption)	Percent of Initial Cu Area (by N ₂ O decomposition)
0	100	100
5	88	107
40	87	115

^a 33 vol% CO, 2 vol% CO₂, balance H₂, < 80 ppb H₂S. Flow rate: 100 cm³/min.

Catalyst mass: 0.0178 g



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FIGURE 3-1 LOSS OF SURFACE AREA OF COPPER AND ZINC OXIDE COMPONENTS OF C79-1 CATALYST DURING EXPOSURE TO 5 ppm H₂S IN SYNTHESIS GAS

Composition: 33 Vol% CO, 2 Vol% CO₂, Balance H₂; T = 573 K; P = 1 atm;
0.0178 g. Catalyst; Gas Flow Rate: 100 cm³/min.