

Effect of Reduction Conditions upon Metal Area in CuO-ZnO Catalyst

The mixed oxide of copper and zinc is used as a catalyst for the water gas shift reaction. Prior to reaction the catalyst is activated by treatment with reducing gas mixtures for converting copper oxide to metallic copper. It has been observed that not only factors like method of preparation, curing temperature, nature of support, etc. but also conditions of reduction affect the activity and stability of copper-zinc oxide catalyst for shift reaction. The present work deals with the determination of the metal area after reducing the catalyst under different conditions.

The catalyst used was a commercial variety prepared by coprecipitation of hydroxides from mixed nitrate solutions. The hydroxides were dried at 110°C, pelleted, and cured at 350°C. The copper oxide content was found to be 33.8%. A mixture of hydrogen and nitrogen was passed through De-oxo catalyst for removing oxygen and through silica gel for drying. Carbon monoxide was prepared from formic acid and concentrated sulfuric acid and freed from carbon dioxide and oxygen by passing through a KOH solution and alkaline pyragallol; for reduction in the presence of steam the reducing gas (CO or H₂) was passed through a saturator at 90°C to attain a steam: gas ratio of 3. Nitrous oxide was purified by repeated freezing at liquid nitrogen temperature and thawing in vacuum.

About 1 g of the catalyst (-18 + 30 mesh) mixed with the same quantity of Pyrex glass chips of the same size was taken in a reactor tube (Fig. 1a) attached to a volumetric adsorption apparatus. Gas mixtures consisting of H₂ + N₂, CO + N₂, H₂ + steam, and CO + steam were used for the reduction of the catalyst. Reductions were carried out at 175, 200, and 225°C, respectively. The catalyst was heated slowly in a

stream of N₂ (2.5 liters/hr) to the desired temperature and gradually N₂ was replaced by the reducing gas. The total time of reduction was 2 hr.

After reduction the catalyst was evacuated for 3 hr at a temperature 10°C higher than the temperature of reduction and to a pressure of 10⁻⁵ Torr. The catalyst was then cooled to the desired temperature for nitrous oxide decomposition and a known pressure of nitrous oxide was introduced in the sample tube. The decomposition reaction was interrupted after different intervals of time by freezing the unreacted nitrous oxide in a U-tube trap cooled in liquid nitrogen; the pressure of nitrogen formed was noted. After pumping out nitrogen, the liquid nitrogen bath was removed and a fresh dose of nitrous oxide was introduced.

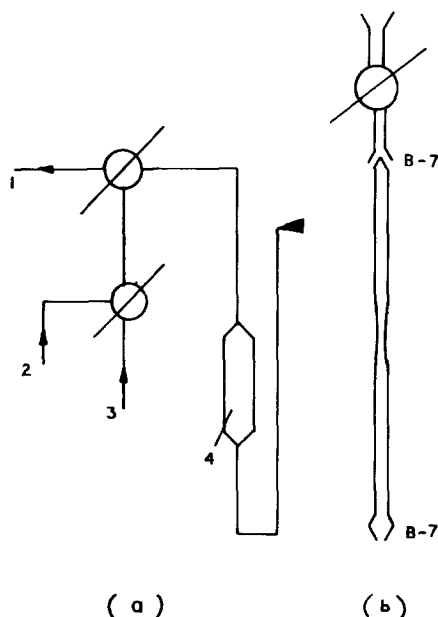


FIG. 1. (a) Arrangement for the measurement of N₂O decomposition. (1) To vacuum manifold. (2) Inlet for steam + gas. (3) Inlet for dry gas. (4) Thermocouple pocket. (b) Sample tube for ESR measurements.

In this way the decomposition was studied at various pressures and temperatures and for different times of contact. It was found that the amount of nitrous oxide decomposed attains a saturation value at a pressure of 200 Torr and a contact time of 12 hr. The effect of temperature can be seen from Fig. 2.

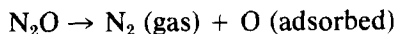
For copper particle size measurement by X ray the catalyst was ground and sieved to -300 mesh size and mixed with an equal volume of quartz powder of the same size. About 0.5 g of this mixture was taken in a small reactor tube provided with a side arm. The catalyst was reduced following the same procedure as described before. After reduction the reactor tube was evacuated and sealed. A part of the catalyst was transferred to the side arm which was sealed out. The tip of the sealed capsule was dipped into collodion solution and broken so that all of the reduced catalyst was covered with a protective coating of collodion. The X ray measurements were then carried out using a Guinier Camera.

For ESR measurements the catalyst + quartz mixture was reduced in hydrogen in a quartz tube as shown in Fig. 1b. After reduction the stopcock was closed and the exit was sealed. The ESR spectra of the reduced catalyst was then determined. The tube was again attached to the adsorption apparatus and left in contact with nitrous

oxide for 12 hr; following that, another measurement of the ESR spectra of the oxidized catalyst was carried out.

Total surface area of the reduced catalyst was determined by BET method using nitrogen as an adsorbate.

Decomposition of nitrous oxide on both supported and unsupported catalysts have been studied by Scholten and Konvalinka (1) and Osinga *et al.* (2). The decomposition is accompanied by desorption of nitrogen and uptake of oxygen by copper surface.



It is possible to measure the surface area of copper from the amount of nitrogen formed if (a) the degree of coverage by oxygen atoms and (b) the stoichiometry O/Cu or the nature of adsorbed oxygen ions are known. For parameter (a), Scholten and Konvalinka have shown that $\theta \approx 1$ for a pressure of 200 Torr of nitrous oxide at 90–100°C. Under identical conditions Osinga *et al.* found $\theta \approx 0.35$. Thus the degree of coverage under the same conditions of temperature and pressure will depend upon the nature of the support and should be determined separately for each type of catalyst. In the present investigation it can be seen from Fig. 2 that the amount of nitrogen formed increased slightly when the temperature is increased from 30 to 70°C. Above 70°C there is a sharp increase in decomposition indicating onset of bulk oxidation (1). It can be concluded, therefore, that for this particular copper catalyst $\theta \approx 1$ at 30°C.

The O/Cu ratio has been assumed to be 1/2 by Scholten and Konvalinka (1). The average surface concentration of copper atoms in metallic copper being 1.78×10^{15} it is possible to calculate the copper area. In the present investigation the metal surface area has been calculated from the area of cross section of the adsorbed oxygen which can be present as either O^- or O^{2-} or both. ESR measurement of reduced and evacuated catalyst showed too much microwave absorption due to the presence of a large

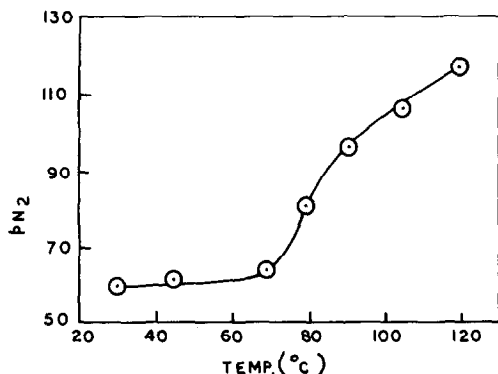


FIG. 2. Effect of temperature on N_2O decomposition. (Pressure of N_2O , 200 mm; time of contact, 12 hr.)

TABLE I

| Reducing medium | Reduction temperature (°C) | BET surface area (m ² /g cat) | Copper surface area (m ² /g cat) | Copper crystallite size (Å) | |
|------------------------|----------------------------|--|---|-------------------------------------|--------------------------|
| | | | | From N ₂ O decomposition | From X ray decomposition |
| H ₂ | 180 | 26.7 | 16.2 | 140 | 150 |
| | 200 | 22.0 | 14.1 | — | — |
| | 230 | 16.0 | 15.0 | 151 | 180 |
| H ₂ + steam | 180 | 18.1 | 15.4 | — | 130 |
| | 200 | 19.0 | 12.0 | — | — |
| | 230 | 20.0 | 11.0 | — | 180 |
| CO | 180 | 17.9 | 15.5 | — | — |
| | 200 | 18.2 | 15.7 | — | — |
| | 230 | 19.0 | 15.5 | 147 | — |
| CO + steam | 180 | 19.8 | 8.0 | — | — |
| | 200 | 19.6 | 11.5 | — | 150 |
| | 230 | 19.1 | 11.1 | — | — |

amount of metal in the solid. Treatment with nitrous oxide decreased the absorption and the spectra could be recorded. However, no signal due to O⁻ was observed indicating that the adsorbed oxygen is present as O²⁻ ion. Taking the ionic radii of O²⁻ ion as 1.32 Å (3) it is possible to calculate the metal area (Table I).

It can be seen that on reduction in the presence of steam there is a decrease in metal area. This is due to partial oxidation of the metal surface by steam (4). Retreatment of the H₂ + steam or CO + steam reduced samples with dry H₂ increases the metal area.

Particle size of copper in five reduced samples have also been measured by X ray. The values thus obtained agrees fairly well with that calculated from nitrous oxide decomposition.

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