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Uniformity of Supported CuO from Rate of Reduction with Hydrogen*

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Rates of reduction of supported cupric oxide catalysts with hydrogen are described. An induction period precedes a stage of maximum rate, after which the rate declines. The induction period is interpreted in terms of the growth of nuclei of metallic copper, and has associated with it an activation energy of 26 kcal/mole. Reduction in the maximum rate stage and beyond is first order in hydrogen, usually first order in unreduced cupric oxide, and has an activation energy of 12 kcal/mole. The data are consistent with a reaction at the Cu-CuO interface, with little participation of a Cu_2O stage. From the percentage of the oxide that participates in the first-order rate, the uniformity of the supported CuO can be judged. This is high for silicon carbide, tabular (α) alumina, diatomite, and magnesia supports, and somewhat lower for glass or silica. γ-Alumina and zeolite show low uniformity, and it is probable that much copper oxide is chemically combined with these supports.

INTRODUCTION

Supported metals or metal oxides are widely used as catalysts, and in this use the nature of the exposed solid phase is of great interest. One way to study this phase is to observe its rate of reaction with a gas, as in the reduction of a supported metal oxide. The reduction of a metal oxide with hydrogen is an interesting topochemical reaction, not fully understood in its own right, but still capable of supplying a great deal of information. Reduction rates can tell something about the activity of a surface phase as well as about the uniformity of the supported oxide. Such measurements have not been widely used in the study of solid catalysts, yet they have real potential as supplements to physical methods of examination.

If the reduction reaction bears some relationship to the catalyzed reaction, rates of reduction may have a bearing on catalytic mechanism. Thus the rate of reduction of cupric oxide with hydrogen has some significance with respect to the $H_2 + \frac{1}{2}O_2$ reaction over CuO. In the present paper we report rates of reduction of supported cupric oxide catalysts of various types. The primary purpose of these is to tell us something about the state of combination or dispersion of the cupric oxide.

Many studies of reduction of unsupported CuO with H_2 are reported in the literature. An early study is that of Wright *et al.* (*1*) who showed that the reaction started with an induction period, increased to a maximum rate, and then declined. Recent studies are those of Bond and Clark (*2*) and Boldyrev and Ermolaev (*3*), as well as others to be cited later. Much has been learned in these studies, but there is not full agreement as to the order in hydrogen, the effects of water vapor, or the influence of introduced copper nuclei. In many respects supporting CuO on a truly inert material aids the study of the reaction, for it diminishes the tendency toward sintering.

EXPERIMENTAL

Measurements of reduction rate were made by observing the pressure drop in a

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closed system filled with circulating hydrogen at about 300–600 mm. The catalyst granules or pellets were placed in a glass tube 15- or 20-mm ID (7.5 mm for catalyst 9.) that was heated in an electric furnace. An equal volume of quartz chips above the catalyst served as a preheating zone. Aside from the reactor tube, the remainder of the system was at room temperature. Hydrogen was circulated by an all-glass, double-acting reciprocating pump, similar to those described by Livingston (*4*) and by Brunfeldt and Holm (*5*). The total system volume was 738 cc in some experiments, and 941 cc in others. Weights of catalyst varied from 2 to 24 g, depending on Cu content. The gas circulation rate exceeded 2 liters/min so that the full circle was completed in less than 30 sec. Flow was from the top to the bottom of the catalyst tube. Just below the furnace was a trap containing Drierite and Ascarite. The trap and the rapid circulation kept the water content of the hydrogen to a low and nearly constant level. The system was quite similar to that recently used by Delmon (*6*) for NiO reduction.

To avoid contamination with mercury, which has been shown (*7*) to seriously poison copper catalysts, a liquid nitrogen trap was placed between the system and the adjacent vacuum pump, while pressure was read by means of a 12-inch diameter, Heise, Bourdon-tube gauge. This gauge had a scale from 0–800 mm (Hg) vacuum relative to atmospheric pressure, and could be read to 0.5 mm. The tube of the gauge had a volume of about 50 cc, and therefore a portion of the circulating gas was constantly passed through it by means of a flexible connection at the normally closed end. A bypass around the catalyst tube permitted the bulk of the system to be filled with hydrogen at a known pressure. The hydrogen could be rapidly expanded into the catalyst tube to give a known initial pressure.

The normal procedure was to load the catalyst, evacuate to 10^{-5} mm, test for absence of leaks, heat the furnace to the desired temperature, introduce hydrogen (purified over hot copper, Drierite, and a liquid nitrogen trap) into the circulating system, expand hydrogen into the reactor at time zero, set the pump to give a constant circulation rate, and then follow the system pressure as a function of time. Instantaneous rates were calculated from readings taken at intervals of 0.5 to 20 min, depending on rate.

Catalysts

1. CuO. Cupric hydroxide was precipitated at 100°C from sulfate solution with ammonia, washed, and heated to boiling in NaOH solution to convert to the black oxide. The oxide was washed, dried at 110°C, and broken to 10–20 mesh granules.

2. CuO/SiC, 1.8% Cu. Granular silicon carbide porous aggregates, 8–10 mesh, from the Carborundum Co., were impregnated with cupric nitrate, dried, and calcined in air 4 hr at 450°C.

3. CuO/T-71 alumina, 1.3% Cu. Tabular alumina (α-alumina), Type T-71, from the Aluminum Co. of America, was washed with hot aqueous hydrochloric and nitric acids and water. The 8–14 mesh granules were plated with metallic copper at 40°C. The plating solution had been prepared by dissolving cupric acetate in water, adding ammonia solution until the precipitate first formed was redissolved, and then adding hydrazine hydrate solution. The granules were washed, dried, and calcined 2 hr at 350°C in air.

4. CuO/T-71 alumina, 1.88% Cu. Prepared as catalyst 3. but with more Cu.

5. CuO/Celite VIII, 14.4% Cu. Johns-Manville Celite VIII bonded diatomite pellets, 5/32-inch diameter, were washed with hot aqueous hydrochloric and phosphoric acids and water, impregnated with cupric nitrate solution, dried, and calcined in air 4 hr at 450°C. The support area was 7.5 m^2/g.

6. CuO/glass beads, 0.33% Cu. Beads of 3 mm diameter were washed with hot aqueous HCl and HNO_3, washed with water, plated with Cu as for catalyst 3., washed, dried, and oxidized 1.5 hr at 350°C in air.

7. CuO/SiO_2 gel, 11.7% Cu. A large-pore silica gel was prepared by L. B. Ryland of

these laboratories by adding sodium silicate solution to aqueous HCl and adjusting the pH to 8.0. The gel was washed with 0.75 *N* HCl and water and dried at 120°C. Granules, 14–28 mesh, were treated for 19 hr with a solution 0.2 *M* in cupric nitrate and 1 *N* in ammonium hydroxide; they were then washed, dried, and calcined 4 hr at 450°C in air. A sample of the gel, calcined after drying at 120°C, had a surface area of about 500 m^2/g and a pore volume of 0.84 cc/g.

8. CuO/Alcoa A alumina, ca. 2% Cu. Grade A alumina (now called F-1) from the Aluminum Co. of America, largely a γ-alumina of about 200 m^2/g area, was soaked for 5 hr in a copper–ammonia solution as used for catalyst 7. The 8–14 mesh granules were washed, dried, and calcined 4 hr at 450°C in air.

9. CuO/zeolite, 5.1% Cu. A synthetic zeolite was prepared of formula $NH_4AlSi_4O_{10}$ by L. B. Ryland by hydrolyzing aluminum chloride in the presence of a silica sol, bringing the slurry to pH 11.45, washing the precipitate free of chloride, treating with ammonium chloride solution, again washing, and then drying at 120°C. The NH_3 content was 5.6%. A portion calcined at this stage had area about 300 m^2/g. For impregnation with Cu, 14–28 mesh granules of the dried material were treated for 18 hr with a copper–ammonia solution as for catalyst 7. The product was washed, dried, and calcined 4 hr at 450°C in air.

10. CuO/MgO, coprecipitated, about 14% Cu. A mixture of 1 liter 0.3 *M* cupric nitrate solution and 5 liters of 0.3 *M* magnesium nitrate was added to 7.72 liters of 1 *N* NaOH. The precipitate was filtered, washed, dried 80 hr at 130°C, and calcined 4 hr at 300°C in air. It was used as 8–14 mesh granules.

RATE OF REDUCTION

Figure 1 shows a typical reduction curve. There is an induction period of accelerating rate, and then a period of gradual approach to completion. These two periods are treated separately in the following. However, the rate of reduction can be defined in the same manner for both. Differential rates are used, since they are much more informative than integral reaction curves. Let x equal the fraction of CuO reduced. If $(CuO)_0$ and (CuO) are the initial and later molar quantities of CuO, then $x = [(CuO)_0 - (CuO)]/(CuO)_0$. Rate of reduction is defined as dx/Pdt, where P is the hydrogen pressure in atmospheres, and t is time in minutes. This definition makes use of the first-order dependence on hydrogen pressure, to be mentioned later. For our system the rate is calculated from pressure readings at the start and end of a small time interval:

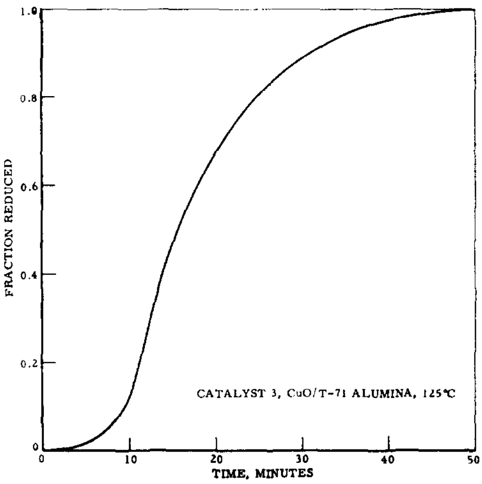

Fig. 1. Typical reduction curve.

$$\text{Rate} = dx/Pdt = \frac{\Delta P}{\Delta t(P_0 - P_e)P_{\text{avg}}}$$

Here P_0 and P_e are initial and final pressures for the entire reduction, while P_{avg} is the average for the time interval. The volume of the system and the sample weight cancel out in the derivation of this formula. An average x is computed for the same time interval used for the rate. P_e is measured in the system, usually by bringing reduction to completion at a higher temperature than that used for the rate measurements. For catalyst 7, P_e was based on the analysis. For the others, $P_0 - P_e$ agreed closely with analyses when available (five cases). It was particularly important to use an experimental P_e when prior oxidation of the catalyst was incomplete.

It will be noted that there is no break in the curve of Fig. 1 corresponding to reduction to the Cu_2O stage. This is in agreement with most of the literature on CuO reduction (*8*), though it differs with a recent paper (*9*) which indicates that no more CuO is present after about 50% reduction. It is possible that differences in reduction conditions can account for appearance of Cu_2O in some cases and not in others. In our work, in one experiment with CuO/T-71 alumina, the reduction was stopped at the halfway point, and a magnetic analysis was made of the catalyst. The susceptibility indicated the presence of CuO equal to about one-half of the original. A check was made to show that this susceptibility did not come from the support.

The maximum rate of reduction, reached at the end of the induction period, depends on the pretreatment of the catalyst. A few catalysts were given various cyclical treatments to study effects on rate. Here a cycle is defined as reduction by hydrogen followed by oxidation by oxygen or air. The oxidation has to be carefully controlled, for unlike the reduction, it starts very rapidly and then slows down markedly with time. Oxidations were started at 150°C or below, but were usually raised to 350°C for completion. Total time of oxidation was about 2 hr. Reproducibilities of rates in a series of standard cycles with CuO/Celite VIII (catalyst 5.) were quite good (Table 1).

TABLE 1
DUPLICATE REDUCTIONS AT 120°C FOR CATALYST 5

Cycle No.	Max. rate (fraction/min × atm)
9	0.058
10	0.060
13	0.057
16	0.053
18	0.056
20	0.054

The rate increased for the first three or four cycles and then became constant. Maximum rates, obtained at $x = 0.5$ for this catalyst, were corrected for minor deviations of temperature from 120°C.

Effects of circulation rate and of hydrogen pressure were each determined by making abrupt changes while near the maximum rate region. An increase of circulation rate by a factor of three had no effect on the rate. Doubling H_2 pressure doubled the rate. This was tried in two runs, cycles 5 and 6 of a series with catalyst 5.; calculation gave an order of 1.0 ± 0.1. A rate first order in hydrogen has been reported for pure CuO by Chufarov *et al.* (*10*).

Temperature coefficients of the reduction rate were obtained by carrying out reductions at different temperatures (Table 2). In each case the run was preceded by a standard cycle with oxidation terminating at 350°C. From the data in Table 2 an activation energy of 12 kcal/mole is obtained.

TABLE 2
TEMPERATURE EFFECT ON MAXIMUM RATE, CATALYST 5

Temp. (°C)	Cycle No.	Rate (fraction/min × atm)
90	11	0.016
120	9, 18	0.058, 0.056
150	6	0.171

Oxidation at a higher temperature than 350°C caused subsequent reduction to be slower, while oxidation at a lower temperature caused it to be faster. A standard oxidation at 350°C following one of these cycles restored the catalyst to its original condition, as judged by subsequent rate of reduction. However, heating the reduced catalyst to 450°C in vacuum or hydrogen prior to oxidation caused a lowering of later rates which was in part irreversible. The effect of oxidation temperature can be explained by the perfection of the CuO crystallites; a low oxidation temperature leaves imperfect crystals, probably rich in Cu nuclei. Heating effects on reduced catalysts are attributed to sintering of the porous copper.

INDUCTION PERIOD

The accelerating rate in the induction period has been noted many times in the literature on reduction of pure CuO. The same effect is observed with most of the supported copper catalysts. The explanation is that reaction occurs at the interface between the Cu islands and the surrounding CuO. The islands grow from nuclei that form at more or less random sites, probably associated with crystal defects. As the islands grow, the rate increases. The hydrogen is presumed to chemisorb on the Cu and to migrate to the interface where reaction occurs. Chemisorption of H_2 on Cu at elevated temperature has been shown by Kwan (*11*). This simple picture explains well the rate increase in the induction period. Let n be the number of nuclei of Cu per mole of CuO that form early in the reduction, and r the radius of a flat island at time t. Then the rate (assumed also to depend on hydrogen pressure) will be

$$-d(\mathrm{CuO})/dt = kPn(\mathrm{CuO})_0 r$$

Because the reaction is at the interface and is proportional to the length of the interface, r increases linearly with time as long as the islands do not overlap. Thus $r = ckt$, where c is a constant, and $-d(\mathrm{CuO})/dt = ck^2Pn(\mathrm{CuO})_0 t$. Or, since $-d(\mathrm{CuO})/(\mathrm{CuO})_0 = dx$, $dx/Pdt = \text{rate} = ck^2nt$, i.e., the rate increases linearly with time. This equation may be integrated to get an equation of the form $x^{1/2} = k't$. Plots of $x^{1/2}$ vs. t are, indeed, linear in the induction period, but it is more revealing to plot instantaneous rate vs. t. Figure 2 shows this for three reductions of CuO/Celite VIII (catalyst 5). The catalyst had been oxidized at 250°, 350°, and 450°C prior to the reductions, and the rates decrease in that order, both in induction period and at the maximum. For all three runs, rate increases linearly with time up to a certain point, as required by the theory.

Rate constants in the induction period, defined by ck^2n, were measured at three temperatures for catalyst 5. An Arrhenius plot gave an activation energy of 26 kcal/mole. This is in moderate agreement with the activation energy of 12 kcal/mole found for the maximum rate period ($x = 0.5$) of the same catalyst; for if n, the number of nuclei, does not depend strongly on temperature, the activation energy for the induction period rate constant (ck^2n) should be twice that for the period where islands are no longer growing (the rate constant is then of the form $c'k$).

The induction period for pure CuO has sometimes been attributed to removal of water (*8*), since water vapor is known to inhibit reduction. It is more likely, however, that some drying treatments (evacuation) have caused nucleation. In one experiment catalyst 5 was heated in dry oxygen at 500°C for 4 hr. The induction period was even more pronounced than usual.

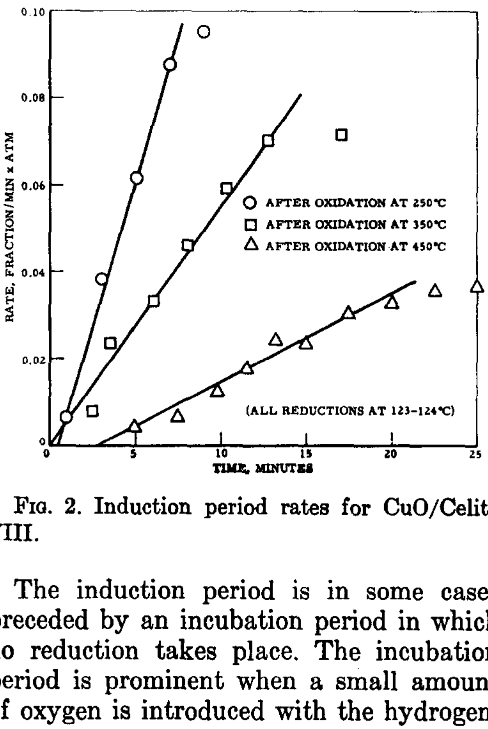

FIG. 2. Induction period rates for CuO/Celite VIII.

The induction period is in some cases preceded by an incubation period in which no reduction takes place. The incubation period is prominent when a small amount of oxygen is introduced with the hydrogen. It appears that the oxygen prevents Cu nuclei from forming, and that until the oxygen is consumed by slow reaction with the hydrogen there is no reduction of the CuO. Thus, 20 mm of air added to 575 mm of hydrogen caused a 20 min incubation period in the reduction of catalyst 5 at 150°C. After the incubation period, the rate increased in a normal induction period.

DECLINING RATE PERIOD

In this paper the declining rate period is used to judge the uniformity of the supported copper oxide. Plots of instantaneous rates against the fraction reduced are shown in Figs. 3 to 6. We have included a curve for coprecipitated CuO-MgO from Christiansen and Huffman (*12*). It is evident that various behaviors are displayed. However, from a total of 11 materials, 7 show first-order behavior in the later part of the reduction; i.e., there is a linear decline in rate as x increases. The pure CuO and CuO/Celite VIII can also be interpreted in this way, leaving only the γ-alumina and zeolite supported materials as exceptions. These can be explained by partial chemical combination of the CuO, as noted later. Thus we shall interpret the reduction for uniform CuO as following a rate law first order in unreduced oxide in the declining rate period. This enables us to judge the uniformity of the supported CuO by the percentage that does not participate in this first-order decline.

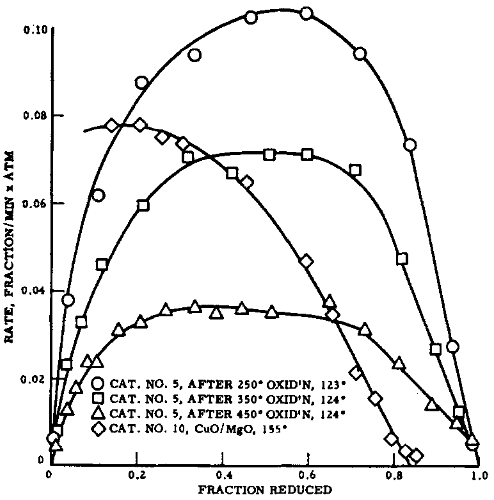

FIG. 3. Reduction rates, CuO/Celite VIII and CuO/MgO.

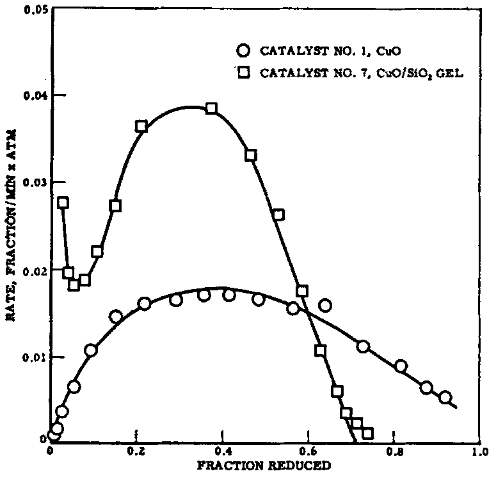

FIG. 4. Reduction rates, CuO and CuO/SiO$_2$ gel (90°C and 148°C, resp.).

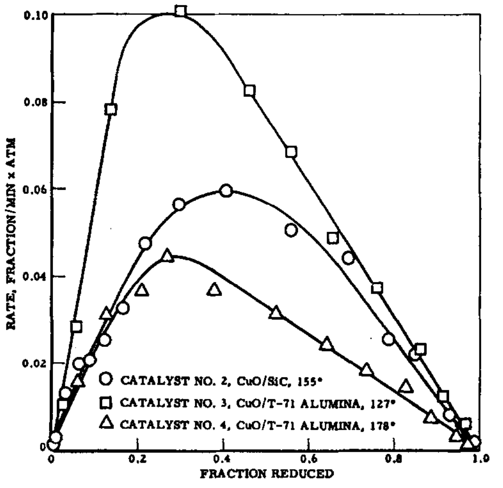

FIG. 5. Reduction rates, CuO/SiC and CuO/T-71 Al$_2$O$_3$.

Several theories have been proposed for first-order declines of solid state reactions of this type (*13*). The phenomena are too little understood and too complex for a simple theory, and will involve the distri-

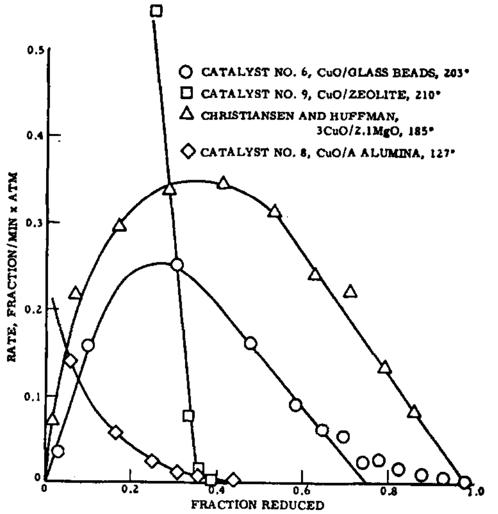

FIG. 6. Reduction rates, various CuO catalysts.

bution of particle sizes, among other things. Mampel (*14*) has shown that overlapping spherical nuclei of copper around which reduction proceeds will lead to a first-order law with small particles in the later stages. A different theory, based on slow diffusion of gas in solid particles has been proposed by Dunoyer (*15*). Since it is clear that copper does not form a protective sheath around the reducing particles of CuO and since diffusion of hydrogen is rapid in porous particles, we favor a theory such as that of Mampel.

TABLE 3

SUMMARY OF REDUCTION RATE MEASUREMENTS

Catalyst No.	Support	(Wt %)[a] Cu	Number of previous cycles	Temp. of last oxidation	Temp. of rate meas.	Max. rate (fraction/min × atm)		Percentage of CuO by "first order"
						At temp. of meas.	At 120°C	
1	None	73.5	0	110	90	0.0173	0.062	100
2	SiC	1.7	0	450	155	0.059	0.017	100
3	T-71 Al_2O_3	1.3	2	350	127	0.101	0.076	100
4	T-71 Al_2O_3	1.66	0	350	178	0.046	0.0064	100
5	Celite VIII	9.8	8	350	124	0.071	0.060	100
6	Glass beads	0.33	0	350	203	0.25	0.017	75
7	SiO_2 gel	11.7[b]	0	450	148	0.038	0.014	71
8	A-Alumina	1.6	1	310	127	(0.14)	(0.10)	(28)
9	Zeolite	5.1	1	250	210	(0.80)	(0.046)	(37)
10	MgO	13.7	1	300	155	0.078	0.022	84
C & H[c]	MgO	33.6	0	200	185	0.35	0.040	97

[a] Equivalent to CuO indicated by hydrogen to completely reduce.

[b] From analysis.

[c] From reference (*12*).

Table 3 summarizes the rate data for various materials. We shall discuss them individually. Unsupported CuO (Fig. 4) gave a rate curve similar to those reported by Bond and Clark (*2*). Although only the last 40% of the reduction shows a linear decline, we consider this material to be uniform, by definition. There is no tail on the reduction curve. There is a nearly constant rate from 0.2 to 0.6 reduction. Bond and Clark presented a theoretical rate equation, with two empirical constants, which was based on a modification of the Prout-Tomkins mechanism (*13, 16*). In integral form this fitted some of their reductions, carried out at $P = 1$, from about 5-85% reduction. Their equation, in differential form, gives $dx/Pdt = k''(0.3 + x)(1 - x)$. This fits our CuO curve from 20-95% reduction, but it does not fit the data for supported catalysts as well. Since the first-order assumption, $dx/Pdt = c'k(1 - x)$, is simpler, has fewer empirical constants, and agrees better for the supported oxide, it is preferred here. It may be noted that pure CuO was more difficult to work with than the supported material. It did not reoxidize smoothly, and after one cycle had shrunk to half its original volume. The supports are of great help in preventing sintering.

CuO/SiC and CuO/T-71 alumina (Fig. 5). These catalysts are based on inert, low-area supports. They act alike, and the reduction is first order in unreduced CuO for for the last 60–70% of the reduction. There is no significant tailing of the rate. We conclude that the CuO on these supports is uniform. Microscopic examination of material from impregnated nitrate (CuO/SiC) shows small crystals of CuO scattered over the surface of the support. The copper-plated catalysts (CuO/T-71) are more completely covered with CuO, but in both cases small crystals are held on a nearly inert surface.

CuO/Celite VIII (Fig. 3) acts much like pure CuO, though the surface area of the support is 7.5 m^2/g. The curves of Fig. 3

differ in maximum rate because of different temperatures of preoxidation, but all are of the same shape. The CuO is considered to be essentially uniform. Microscopic examination again reveals small CuO crystals scattered over the surface or in the crevices.

CuO/glass beads (Fig. 6) shows a definite tail in the rate. By extrapolation of the linear part of the rate, we estimate that the CuO was 75% uniform. The rest probably entered into chemical combination with the glass.

CuO/SiO_2 gel (Fig. 4) was made by the adsorption of a copper–ammonia complex, as described by Kolthoff and Stenger (*17*). Inasmuch as copper put on in this way cannot easily be washed off, it is evidently well distributed over the surface. Furthermore, the amount of copper put on was much less than required to form a monolayer. But according to the rate of reduction the copper was not uniform. About 71% reduced at a first-order rate. Presumably the rest was combined more tightly with the support as a copper silicate.

CuO/A alumina (Fig. 6) was very different in behavior. Here a rapid initial reduction slowed down markedly with time. There was no maximum rate. To complete the reduction it was necessary to raise the temperature to 200°C. The CuO/A alumina in oxidized form was a light blue color. This has also been noted by Selwood and Dallas (*18*). CuO is known to form a spinel with Al_2O_3. A chemical combination is certain here. The data show that approximately 28% of the CuO was more easily reduced than the rest. Mooi and Selwood (*19*) found that copper at low concentration on γ-alumina was less active per unit of copper than at higher concentration.

CuO/zeolite (Fig. 6) was much like the CuO/A alumina in reduction behavior. The reduction started rapidly, slowed down markedly, and tailed off. The temperature was raised to 250°C to complete reduction. Again a chemical combination of the CuO is indicated. This altogether defeated our attempt to obtain a uniform copper on a high-area support by an ion exchange technique.

CuO/MgO (Figs. 3,6) according to a published curve of Christiansen and Huffman (*12*), which we replotted, was nearly 100% uniform. Our preparation contained more MgO than theirs, and was indicated to be 84% uniform. X-ray data of Wagner *et al.* (*20*) indicate that CuO and MgO do not form compounds or solid solutions to an appreciable extent when the mixture is heated to 630°C.

Rates of reduction on a common basis are summarized in the next-to-last column of Table 3. The rates are surprisingly uniform, varying over only a factor of 12. If all had been measured after an equal series of previous cycles they would have been closer. It is probable that in all cases except the silica gel, A alumina, and zeolite supports, we are dealing with CuO crystallites of about the same size and imperfection. The high-area supports do not increase the rates as we might expect, either because the CuO crystals are still about the same size, or else because the chemical combination of the CuO slows reduction.

In summary, we have found that the reduction of supported CuO is an interesting topochemical reaction that deserves study in its own right. Considerable information about uniformity and chemical combination of the CuO is derived from reduction rates.

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