New Data on the Reduction of Copper Oxides by Gaseous Reducing Agents at Low Temperatures \((<100^{\circ})\)

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Abstract

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New Data on the Reduction of Copper Oxides by Gaseous Reducing Agents at Low Temperatures ($< 100°$)

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Continuing (^{1}) our study of the reduction of metal oxides, in determining the lowest temperature at which the reduction of copper oxides by gaseous reducing agents is still possible, we observed a number of phenomena that may be of practical and theoretical interest. In the present work we subjected preparations of copper oxides (CuO and Cu_2O), taken in loose or briquetted form, to reduction—in one case with pure carbon monoxide, and in another with carbon monoxide mixed with other gases. The study was carried out at temperatures on the order of 45–105°, for which purpose a glass apparatus was used, consisting of a reaction vessel with a capacity of 100 ml and a coil for preliminary heating of the gas. The entire system was placed in a glycerin bath, the temperature of which was regulated with an accuracy of ±0.25°. A 2 g sample of the material under investigation was placed in a small glass cup and put into the reaction vessel directly below the opening of the gas-supply tube. The bath was heated to the specified temperature while the system was simultaneously evacuated. When the required temperature and a high vacuum had been reached, gas was admitted into the apparatus, and after the pressure had been equalized to atmospheric pressure the gas was passed through at a rate of 500 cm^3/hour. Every half hour a gas sample was taken and analyzed for CO_2. The residue after reduction was weighed, and from the decrease in the weight of the sample the oxygen loss and the degree of reduction were calculated. Subsequently the residue as a whole, and also separately its inner and outer portions, were subjected to X-ray structural analysis in Cu K_α radiation using a Ni filter.

The experiments performed showed that when the sample was taken in loose form, a denser brick-red lump first formed approximately in the middle of the sample; this lump gradually grew as the degree of reduction increased, and even when nearly complete reduction had occurred the surface of the sample remained covered with black spots. This was especially striking in the case of a briquetted sample, when the dark layer covering the briquette on top differed sharply from the brick-red interior of the briquette, which, according to X-ray structural analysis, consisted only of the metallic phase. This shows that in the given case the reaction begins inside the sample and proceeds as a clearly delimited front from the middle of the sample toward its periphery, so that the

Fig. 1

Figure 1: Fig. 1

last layer to be reduced is the one lying closest to the fresh stream of carbon monoxide. The phenomenon described was repeated in all experiments carried out at temperatures below 140°, and only above this temperature did the red color of the reduced product appear at the beginning of the experiment on the surface of the sample. In all cases the rate of reduction was greater for samples taken in briquetted form (see Fig. 1). This phenomenon is particularly well illustrated by the experiments at 45°, when only briquetted CuO showed signs of reduc-

···reduction, as could be judged not only from the loss in weight of the charge (Table 1), but also from the formation of a thin brick-red band in the middle of the briquette. This phenomenon is also observed in experiments with Cu_2O, in which reduction, if it occurred at all, occurred only in briquetted samples. On X-ray diffraction patterns of residues obtained after brief reduction of CuO, when much unreduced CuO still remained, the presence of a Cu_2O phase was in no case detected, despite the obvious presence of reduced metal. Comparing the kinetic curves for the reduction of CuO at 85 and 105°, one can see that the rate of the process is somewhat higher at the lower temperature (85°), which indicates an indirect dependence of the rate of the process on the temperature at which the investigation is carried out.

Fig. 1

Experiments on the reduction of copper oxides by hydrogen at 85° (Table 2) clearly showed that under these conditions hydrogen has no reducing action on copper oxides. The addition to carbon monoxide of 8% carbon dioxide greatly lengthens the induction period (Fig. 2), but after the reaction has begun, the concentration of CO_2 in the gas phase may reach 75%.

Table 1

No. of samples*	Material	Samples	Temp., °C	Duration of experiment, min.	Weight loss, %	Degree of reduction, %
1	CuO	Bulk	45	360	none	none
2	CuO	Briquette	45	360	1.8	8.95
3	Cu_2O	Bulk	45	360	none	none
4	Cu_2O	Briquette	45	360	none	none
5	CuO	Bulk	65	360	5.08	25.28
6	CuO	Briquette	65	360	8.98	44.66
7	Cu_2O	Bulk	65	360	none	none
8	Cu_2O	Briquette	65	360	none	none

No. of samples*	Material	Samples	Temp., °C	Duration of experiment, min.	Weight loss, %	Degree of reduction, %
9	CuO	Bulk	85	360	17.56	87.33
10	CuO	Briquette	85	360	17.99	89.46
11	Cu_2O	Bulk	85	360	0.17	1.50
12	Cu_2O	Briquette	85	360	5.60	46.16
13	CuO	Briquette	85	180	17.96	89.32
14	Cu_2O	Briquette	85	180	1.40	12.52
15	CuO	Briquette	105	180	17.87	88.87
16	Cu_2O	Briquette	105	180	1.30	11.63

* The sample numbers correspond to the curve numbers in Fig. 1.

Modern theory regards the reduction of metal oxides as two processes—adsorption and autocatalytic ([2]-[4]). Such a formulation of the question cannot in principle raise objections, but it is too general and therefore does not make it possible to explain all the phenomena accompanying this process in particular cases. Thus, there are contradictory opinions ([5]) concerning the reducing activity of hydrogen and cuprous oxide

carbon monoxide. But cases are known in which carbon monoxide reduces oxides at a measurable rate, while hydrogen has no reducing action. The data we have obtained on the possibility of reducing CuO directly to the metal, bypassing the intermediate formation of Cu_2O, contradict the established opinion ([6]) concerning the obligatorily stepwise reduction of CuO. Proceeding from existing concepts of the mechanism of reduction by gaseous reducing agents, it is difficult to explain the fact that in our experiments the previously briquetted specimens were reduced more rapidly, and the process began in the middle of the specimen and proceeded from the center to the periphery. The explanation of the phenomena described must be sought in the fact that the chemisorption of carbon monoxide on copper oxides proceeds by a mechanism in which the active centers are metal ions, with formation of a layer of the type M=C=O, analogous in structure to metal carbonyls. Confirmation of the view that the reduction of copper oxides by carbon monoxide at temperatures at which thermal dissociation of the oxide is still impossible and the stage of formation of carbonyl-like compounds takes place can also be seen in the existing analogy between the processes of reduction and the synthesis and decomposition of metal carbonyls ([7]).

Fig. 2

Proceeding from the foregoing, the mechanism of reduction of copper oxides by carbon monoxide at temperatures below 110° may be represented as follows. At first, selective activated adsorption occurs, in which the carbon monoxide molecules, penetrating into the crystal lattice of the oxide,

Table 2*

Specimen No.**	Material	Added gases	Weight loss, %	Degree of reduction, %
1	CuO	5% O_2	15.40	46.58
2	Cu_2O	5% O_2	3.40	30.41
3	CuO	8% CO_2	16.85	83.75
4	Cu_2O	8% CO_2	1.20	10.75
5	CuO	37% CO_2	0.25	1.24
6	Cu_2O	37% CO_2	none	none
7	CuO	20% H_2	16.77	83.40
8	Cu_2O	20% H_2	2.51	22.45
9	CuO	20% N_2	13.67	67.98
10	Cu_2O	20% N_2	2.30	20.57
11	CuO	99% H_2	none	none
12	CuO	99% H_2	none	none

* Duration of the experiments 180 min.; when hydrogen was used, 360 min.; heating temperature 85°; only briquetted specimens were used.
** Specimen numbers correspond to the numbers of the curves in Fig. 2.

oxide, attach themselves at the nodes of the expanded lattice, which makes possible the formation of a carbonyl complex. The heterogeneous reaction of carbonyl formation occurs wherever carbon monoxide comes into contact with the surface of the starting material. Briquetting of the material cannot compact the powdered copper oxides to such a state as to prevent the access of CO to the very innermost parts of the specimen, especially since before the begi—

the experiment, the system was evacuated to a high vacuum. Therefore, at first, activated adsorption of carbon monoxide occurs uniformly throughout the entire volume of the sample, which also implies uniform carbonyl formation. But after the carbonyl complex has formed, the latter is retained on the surface of the material, and in order for the process to continue, desorption of the carbonyl into the gas phase or decomposition of the latter and desorption of the decomposition products is necessary. Direct synthesis of the carbonyl is accompanied by decomposition of the product, proceeding simultaneously with the ever-increasing rise in temperature. Pure carbon monoxide stabilizes the carbonyl complex, and at the same time the diffusion of CO to the middle of the sample occurs more poorly than to its surface; therefore, decomposition of the carbonyl complex in the middle of the sample is more probable, and the reduction process begins in the inner parts of the sample. The reduction of copper oxides by carbon monoxide proceeds with considerable evolution of heat, especially large when CuO is reduced directly to the metal. A kind of spontaneous acceleration of the reaction occurs, as is well illustrated by the kinetic curves. For the same reasons, the rate of the process drops sharply when the reaction reaches the peripheral parts. Evidently, compaction (briquetting) of the material acts in the same direction, creating conditions under which regions with less heat dissipation are formed.

It is evident from the foregoing that the greatest rate of reduction was achieved at 85°, and not at the highest temperature of our experiments (105°). This can be explained by the fact that, apparently, at this temperature the most favorable combination of conditions is ensured for the occurrence of the individual acts of the process, in particular the formation and decomposition of intermediate carbonyl-like compounds, which are connected with the chemical nature of the reducing agent.

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