

REDUCTION REACTIVITY OF $\text{CuO-Cr}_2\text{O}_3$ MIXED OXIDES WITH HYDROGEN AND THE EFFECT OF GAMMA PRE-IRRADIATION

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ABSTRACT

The physico-chemical properties and parameters of $\text{CuO-Cr}_2\text{O}_3$ mixed oxides as well as their reactivity toward reduction with hydrogen have been investigated by means of various methods (X-ray analysis, electron spectroscopy for chemical analysis (ESCA), DTA, IR spectroscopy and scanning electron microscopy). A series of mixed oxides of various compositions in the range 0–100% of each component were prepared by calcinating the mass of coprecipitated basic carbonates in air. The reduction kinetics were studied by isothermal thermogravimetry in the temperature range 180–470 °C. The effect of the origin of the oxides on the reactivity of the oxide system during its hydrogen reduction was proved by comparing its properties with those of a previously studied series of analogous mixed oxides, which were prepared from different precursors.

The pre-irradiation of the system by ^{60}Co γ radiation results in a positive kinetic effect (an increase in the reduction rate) if the lowest dose applied is 2.57×10^6 Gy. The magnitude of the radiation effect is greatly dependent on the composition of the mixed oxides.

INTRODUCTION

The mixed oxides of transition metals $\text{A}^{\text{II}}\text{O-B}_2^{\text{III}}\text{O}_3$ with the spinel structure are among the most active catalysts for various industrial reactions. Their properties and chemical composition may be affected not only by the type of starting compound, but also by the conditions of thermal decomposition [1,2]. If A is a catalytically active metal and B_2O_3 is a thermodynamically stable non-reducible oxide, the reduction of these systems with hydrogen leads to the metallic catalysts being formed on the oxide carrier. Thus, the above-mentioned factors conspicuously influence the reactivity of mixed oxides during the reduction as well as the catalytic properties of the final products.

In our previous paper [3], we studied the reduction of the mixed oxides $\text{CuO-Cr}_2\text{O}_3$ of various composition which were prepared by the decomposition of mixed crystalline nitrates in air. The aim of the present work was to

investigate the physico-chemical properties of the same series of oxides prepared from different starting salts and to find correlations between these properties, as affected by the different origins of the two series and by the kinetics of their reduction with hydrogen.

The reactivity of some pure oxides including CuO and mixed oxides during reduction may be altered by various sorts of ionizing radiation [4,5]. This effect has not hitherto been sufficiently studied with mixed systems containing a single reducible component, so the influence of γ pre-irradiation on the reduction kinetics of CuO–Cr₂O₃ mixed oxides was also investigated.

EXPERIMENTAL

Mixed oxides with various ratios of the two components in the range 0–100 wt.% were prepared by thermal decomposition of basic carbonate precipitates for 4 h at 400°C in air. Aqueous solutions of Cu(NO₃)₂ · 3H₂O and Cr(NO₃)₃ · 9H₂O (both AR grade) as starting materials were mixed together in the required ratios and then coprecipitated during intensive agitation with a 15% stoichiometric excess of a solution of Na₂CO₃. The concentration of all the solutions was 1 mol l⁻¹. The product of calcination was pulverized and the mesh fraction of 0.1–0.02 mm was separated. The copper content was determined electroanalytically, and the chromium concentration was found iodometrically.

The microstructure of the mixed oxides was investigated by X-ray diffraction on a Dron-3 apparatus using Cr *K* α radiation. The specific surfaces of the samples were measured by low temperature selective adsorption of nitrogen from a nitrogen–hydrogen mixture and their morphology was studied using a JSM-50 A (Jeol) scanning electron microscope. The standard DTA measurement was performed on the Netzsch STA 409-thermoanalyser within the range 20–600°C at a heating rate of 5°C min⁻¹. Selected samples were also investigated by IR spectroscopy and the surface oxidation states of both metals were analysed by ESCA using the Al line as the exciting radiation with $E = 1486.6$ eV at 10⁻⁷ Pa.

A part of the prepared mixed oxides was pre-irradiated with ⁶⁰Co γ radiation in air in doses ranging from 5 × 10⁵ to 2.57 × 10⁶ Gy at a dose rate of 4.02 kGy h⁻¹.

The reduction kinetics were studied by isothermal thermogravimetry in the temperature range 180–470°C under conditions strictly comparable for both series of the initial and radiation-modified mixed oxides. The reduction was followed at a hydrogen flow rate of 56 ml min⁻¹ using a 50 mg sample. Under these conditions, the kinetics and the rate of sample reduction at an arbitrary composition are independent of the flow rate of the reducing gas.

RESULTS AND DISCUSSION

Physico-chemical properties of CuO–Cr₂O₃ mixed oxides

From the results of the chemical analysis (Table 1) and from the IR spectra of the samples of various compositions, it follows that under the conditions used there is quantitative decomposition of the copper and chromium basic carbonates. Their crystallochemical conversion during the calcination in air is connected with the following redox processes. In addition to the oxidation of chromium to a higher valency on forming CrO₃, the copper(II) chromate originates by direct reaction of the two majority oxides in the solid according to the equation



Moreover, the Cu²⁺ ions are partially reduced, or copper(II) oxide can be thermally decomposed to elementary copper. The shape of the 1s oxygen

TABLE 1

Notation and properties of mixed oxides CuO–Cr₂O₃

| Sample | Wt. % | | S_1^a (m ² g ⁻¹) | S_2^b (m ² g ⁻¹) | c^c (mg g ⁻¹) | c_s^d (%) | | | |
|--------|-------|--------------------------------|--|--|--------------------------------|-----------------|------------------|------------------|------------------|
| | CuO | Cr ₂ O ₃ | | | | Cu ⁺ | Cu ²⁺ | Cr ⁶⁺ | Cr ³⁺ |
| 1 | 99.03 | 0.00 | 3.0 | 2.7 | 0.0 | 0 | 100 | – | – |
| 2 | 97.14 | 1.99 | 3.0 | 2.9 | 0.0 | | | | |
| 3 | 95.29 | 3.94 | 4.5 | 3.9 | 6.7 | 0 | 100 | 80 | 20 |
| 4 | 91.11 | 6.54 | 12.2 | 12.0 | 18.1 | | | | |
| 5 | 90.20 | 8.23 | 13.0 | 13.0 | 4.0 | 0 | 100 | 71 | 27 |
| 6 | 88.77 | 10.21 | 17.0 | 13.1 | 3.2 | | | | |
| 7 | 77.29 | 19.92 | 27.2 | 27.2 | 8.4 | 0 | 100 | 37 | 63 |
| 8 | 67.57 | 31.81 | 32.1 | 26.3 | 6.3 | | | | |
| 9 | 59.00 | 40.82 | 30.1 | 30.3 | 6.0 | | | | |
| 10 | 48.71 | 47.16 | 33.9 | 38.8 | 6.0 | 9 | 91 | 22 | 78 |
| 11 | 40.29 | 55.56 | 21.8 | 20.7 | 8.4 | | | | |
| 12 | 28.65 | 62.86 | 18.9 | 19.5 | 22.7 | 17 | 83 | 20 | 80 |
| 13 | 18.75 | 74.58 | 2.5 | 27.2 | 110.8 | | | | |
| 14 | 9.91 | 83.79 | 6.4 | 9.5 | 30.8 | 0 | 100 | 20 | 80 |
| 15 | 7.85 | 90.69 | 6.0 | 10.1 | 51.6 | | | | |
| 16 | 5.73 | 90.18 | 5.8 | 7.4 | 40.1 | 5.5 | 94.5 | 31 | 69 |
| 17 | 4.01 | 88.38 | 6.3 | 7.7 | 43.3 | | | | |
| 18 | 1.79 | 88.47 | 5.0 | 10.2 | 73.4 | | | | |
| 19 | 0.00 | 87.80 | 3.3 | 17.0 | 121.9 | – | – | 25 | 75 |

^a S_1 , specific surfaces of initial mixed oxides.

^b S_2 , specific surfaces of the samples after removal of chromates.

^c c , concentration of chromates.

^d c_s , concentration of surface ions of copper and chromium in various oxidation states determined by ESCA.

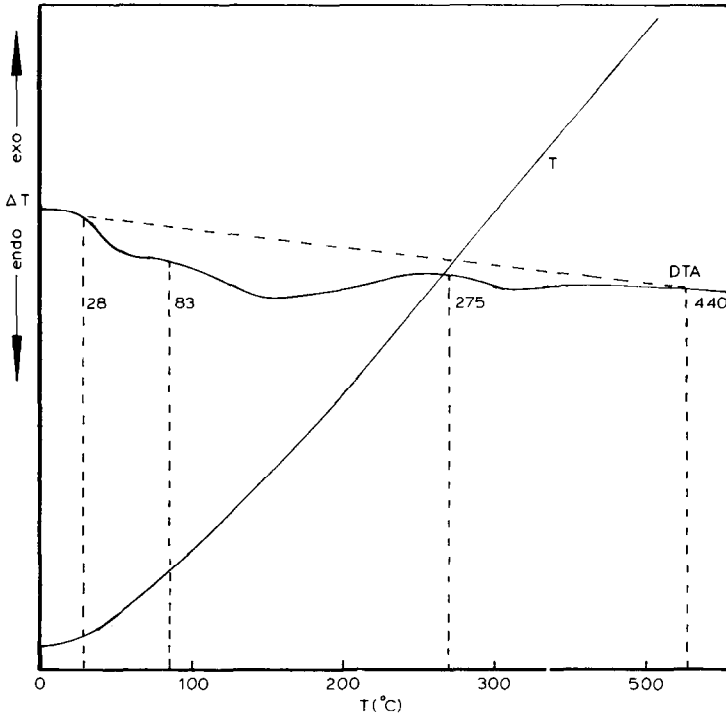


Fig. 1. DTA curve of sample No. 12.

line in the ESCA spectra further proves the presence of adsorbed water or of surface hydroxyl groups in the samples containing an excess of Cr_2O_3 . The broad endothermic effects in the DTA curves of these samples (Fig. 1), including pure Cr_2O_3 , correspond to the decomposition of relatively stable hydrates of Cr_2O_3 with variable composition [6] and to the release of constitutionally bound water.

Owing to the impossibility of the total removal of Na^+ ions by washing of the basic carbonates, the main soluble parts of the calcinated product consist of sodium chromate. Its concentration is by an order of magnitude higher in the region with a pronounced excess of Cr_2O_3 (more than 70 wt.%, see Table 1) and reaches a maximum with pure Cr_2O_3 . Copper(II) chromate, which originates as an intermediate product in the first stage of calcination of a given precursor according to the eqn. (1) is further decomposed to a stable chromite with the spinel structure:



It follows from Table 1 that the magnitude of the specific surfaces depends on the system composition in a non-monotonic manner and achieves its maximum value in the middle of the series with mixed oxides containing the components in the ratio 1:1. From the morphological investigation of

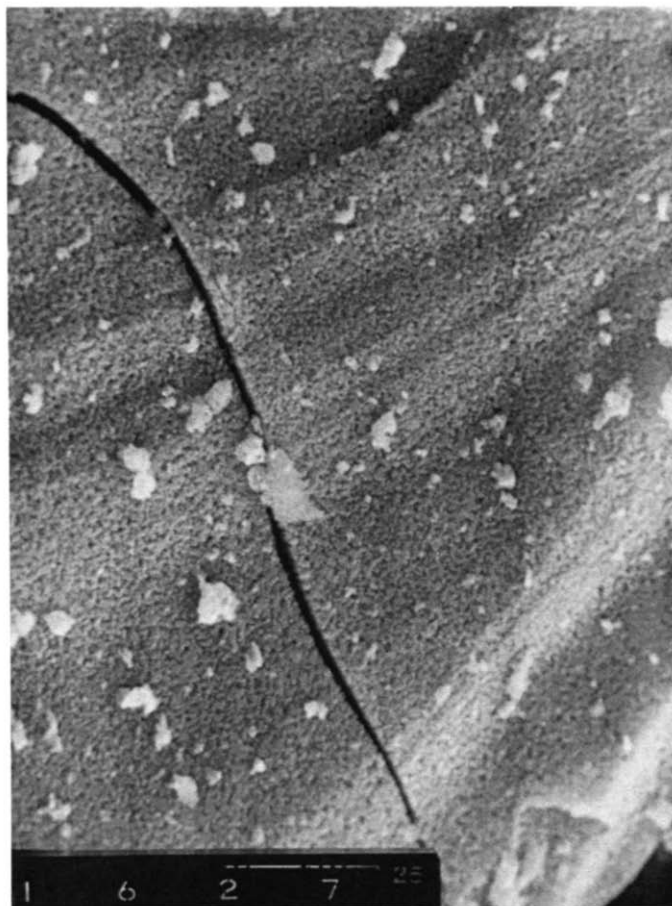


Fig. 2. Electron micrograph of original sample No. 16. Magnification, $3 \times 10^3 \times$; the line segment indicated corresponds to $6 \mu\text{m}$.

the samples, it is evident that the separate phase of chromates associates the individual grains of oxides and decreases the roughness of the surface (Fig. 2). After removing chromates by washing, the grains and their agglomerates are segregated (Fig. 3) and the increasing dispersity is connected with an increase in specific surfaces (Table 1).

X-ray analysis confirmed an independent phase of CuO in the samples 1–4, and with increasing content of Cr_2O_3 , also the presence of selective reflections corresponding to the strong defective cubic structure of CuCr_2O_4 , which transforms to the tetragonal one in sample 11. Samples 12 and 13 show the characteristic lines of Cr_2O_3 and the tetragonal spinel phase. The remaining samples contain only the Cr_2O_3 phase. The extremely broad lines of the cubic CuCr_2O_4 provide evidence for the existence of microstress in the lattice and of the small magnitude of coherent regions (less than 10 nm).

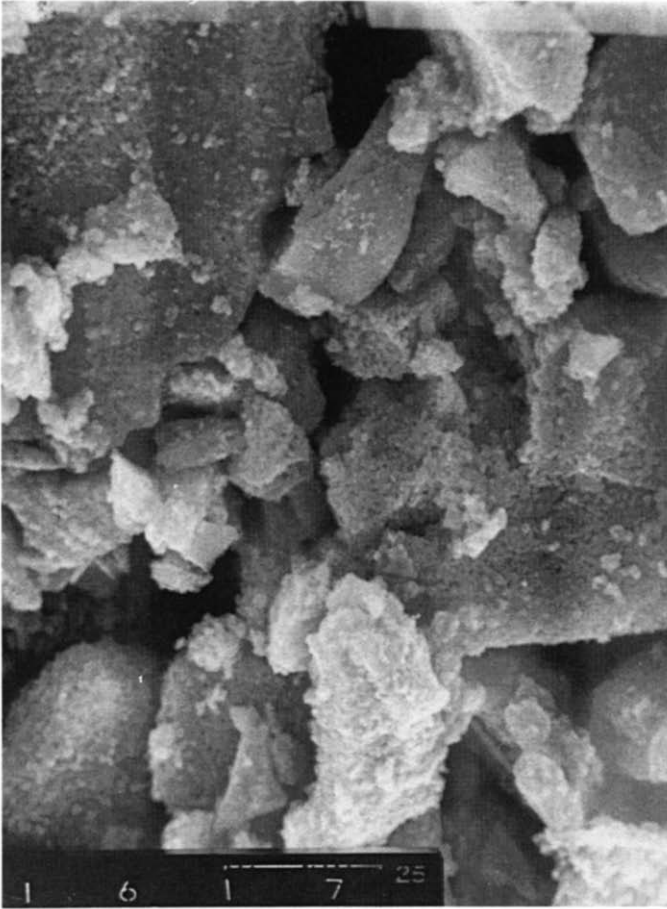


Fig. 3. Electron micrograph of sample No. 16 after washing of chromates and drying. Magnification, $3 \times 10^3 \times$; the line segment indicated corresponds to $6 \mu\text{m}$.

The effect of the origin and of the conditions of preparation of the mixed $\text{CuO-Cr}_2\text{O}_3$ system manifests itself by the formation and by the amount of the spinel phase. With the previously studied analogous system of nitrate origin [3], the presence of chromite CuCr_2O_4 was proved only in those samples whose composition approached the stoichiometric ratio, $\text{Cr}:\text{Cu} = 2:1$. A chromite phase, formed predominantly by reaction (2), was detectable in this case only by IR spectroscopy. Similarly, the quantity of the chromite which originated during additional thermal treatment of the final mixed oxides in an inert atmosphere for 1 h at 700°C by direct reaction in the solid phase according to the reaction



was not detected by X-ray analysis.

For the series of carbonate origin, a similar dominant mechanism of spinel formation can be assumed as in the precipitation and decomposition of copper and chromium hydroxides. In the course of the precipitation of basic carbonates, hydrated compounds of various types [2] are formed, from which the water is gradually split during the calcination and the spinel structure is simultaneously formed. Only the water constitutionally bound into the Cr_2O_3 or minority CrO_3 remains in the system. An analogous effect and a high superstoichiometric oxygen content of chromium sesquioxide in the series under study were not observed with the comparable samples of nitrate origin, where the system passes through the stage of a homogeneous melt during its calcination.

In agreement with the previous results [5,7], none of the physico-chemical parameters followed were affected by γ pre-irradiation in the dose range used.

Reduction kinetics and the influence of γ radiation

From a comparison of the experimental weight losses with the theoretical values for complete reduction of copper oxide, it follows that this oxide is the only reducible component of the system under the conditions used. In contrast with the nitrate series [3], the degree of reduction of CuO , up to its content of 20%, is practically constant (Fig. 4). Kinetic curves for the reduction of samples with the prevailing content of Cr_2O_3 demonstrate the occurrence of several consecutive processes (Fig. 5). The initial, sigmoidal part of the curve corresponds to the reduction of CuO in the mixed oxides. The last part is related to the significant weight loss (Fig. 4) which increases with the reduction temperature (Fig. 5) both with the initial and with the washed samples, including pure Cr_2O_3 . These weight losses cannot be attributed to the reduction of the lattice oxygen of thermodynamically stable Cr_2O_3 , but only to the reduction of all forms of superstoichiometric oxygen of chromium oxides and to the total dehydration of constitutionally bound water in the reducing atmosphere. The initial dark green chromium sesquioxide changes during this treatment to the stoichiometric bright green one.

A different degree of mutual interaction (epitaxial contact) of the two components, determined by the origin and by the conditions of preparation, manifests itself also in the dependences of the reduction rate on the degree of reduction α and on the composition of the mixed system. For the samples of the nitrate series the maximum reduction rate shifts towards lower values of α with increasing Cr_2O_3 content [3], so that the reduction proceeds at the maximum rate in the subsurface grain layers. For the mixed oxides of the carbonate series the position of the maximum reduction rate is independent of the value of α over the whole composition range. The high degree of reduction ($\alpha \approx 0.7\text{--}0.8$), corresponding to the maximum reduction rate of

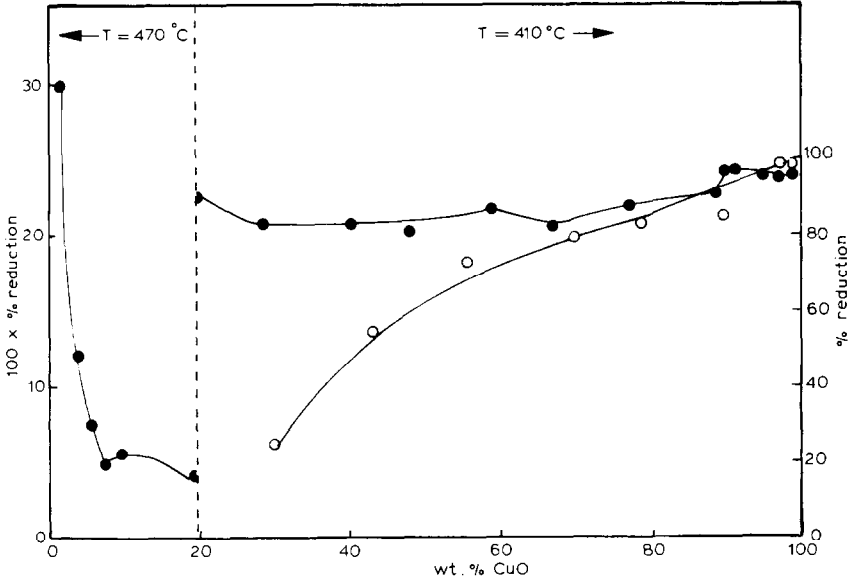


Fig. 4. Dependence of the degree of reduction on the composition at 410 and 470 °C for two composition regions: ●, series of carbonate origin; ○, previously studied series of nitrate origin [3].

the oxides of the carbonate system, can be related to a branched chain mechanism for the spread of the reaction from the grain surface to the bulk of the copper oxide [4].

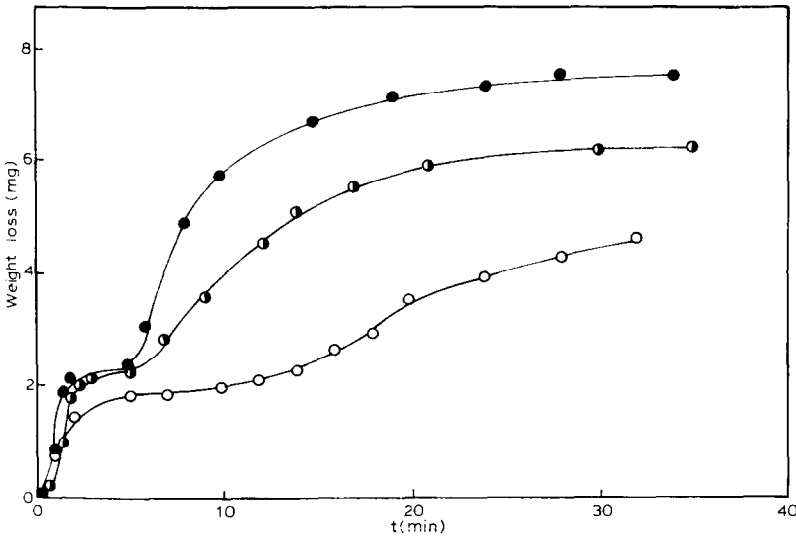


Fig. 5. The variation with time of the reduction of sample No. 13 at various temperatures: ●, 470 °C; ◐, 440 °C; ○, 410 °C.

The retarding effect of Cr_2O_3 as a non-reducible component which blocks the active interface and the nucleation centres of the metal product manifests itself more markedly with the nitrate mixed oxides. Their reduction rate decreases monotonically with increasing amount of Cr_2O_3 up to its content of 30% [3]. Only in the regions of higher Cr_2O_3 concentrations is the reduction accelerated by an active interface of the evolving spinel phase, but the reduction rate of mixed oxides remains lower than that of pure copper oxide.

Figure 6 shows the dependence of the maximum reduction rate of the samples of carbonate origin on the composition. It can be seen that small admixtures of Cr_2O_3 lead to the acceleration of reduction of CuO up to a maximum but with further increases in the content of Cr_2O_3 the rate of reduction decreases. Owing to the strong exothermic character of the reduction of CuO [8], local overheating of the samples takes place [3], so that the process can proceed at higher temperatures in the diffusion regime. This is in accordance with the established lowering of the apparent activation energy of reduction. The mixed oxides, up to a 50% content of Cr_2O_3 were therefore reduced at a low temperature (180°C). From Fig. 7, it is evident that there is an accelerating effect of the Cr_2O_3 admixtures under given conditions. A similar effect was found by Hauffe and Rahmel [9] with the mixed oxides $\text{NiO}-\text{Cr}_2\text{O}_3$ in the region of mutual solubility of the two components (up to 0.6 mol% Cr_2O_3). The positive effect, however, referred only to the initial stage of the reduction proceeding in the surface grain layers, whereas the total reduction time up to a given degree was fourfold

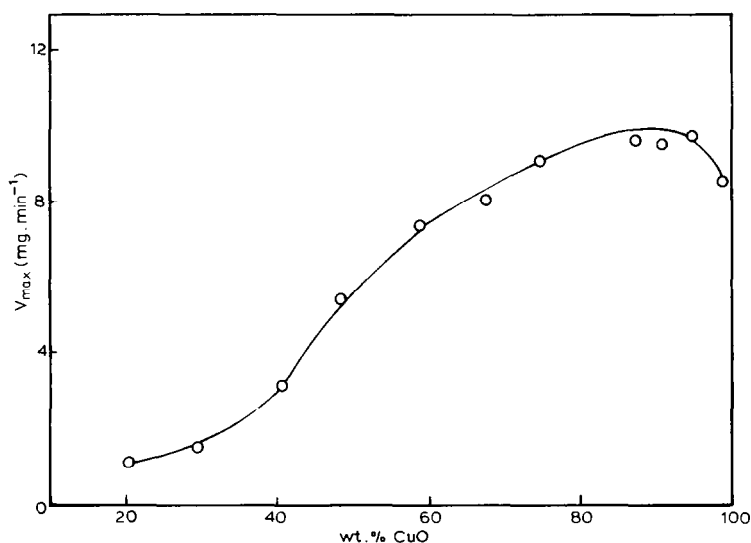


Fig. 6. Dependence of the maximum reduction rate V_{\max} on the composition. Reduction temperature, 290°C .

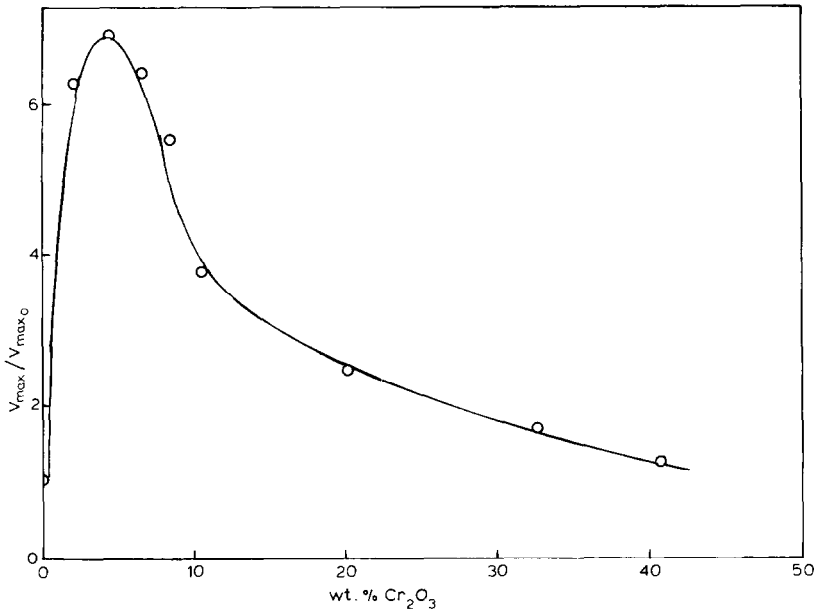


Fig. 7. Plot of the ratio V_{\max}/V_{\max_0} vs. composition. Reduction temperature, 180°C ; V_{\max_0} , maximum reduction rate of pure CuO.

longer in comparison with the reduction of pure nickel oxide. However, in the CuO–Cr₂O₃ system under study, both the surface process and the bulk reaction are accelerated and the total reduction time is shorter as compared with that for the reduction of copper oxide without admixture. The positive effect caused by the admixture of Cr₂O₃ is probably related to the lattice deformations and microstress which lead to a weakening of the metal–O bond in the copper oxide and to the presence of a defective spinel structure. Within the boundaries of the present phases a high concentration of lattice defects can be assumed, which generally accelerate the decomposition processes of the solid. With increasing free Cr₂O₃ content, its retarding effect starts to play a prevailing role and the reduction rate decreases further.

The fact that with the mixed oxides of up to 20 wt.% CuO all this oxide is totally reduced is consistent with a study of the secondary reduction of reoxidized oxides, i.e. the samples which were, after primary reduction, oxidized by air oxygen up to a constant degree and then reduced again at the same temperature. In all cases a slow oxidation of the product of primary reduction proceeds to a lower degree than that corresponding to the total oxidation. By this process, therefore, the compact oxide layer which passivates the grain surface is formed. The residual metallic copper, as a product of primary reduction, is inert, so that it affects neither the rate of nucleation nor the kinetics of the secondary reduction. The degree of secondary reduction corresponds exactly to the previous oxidation. With the

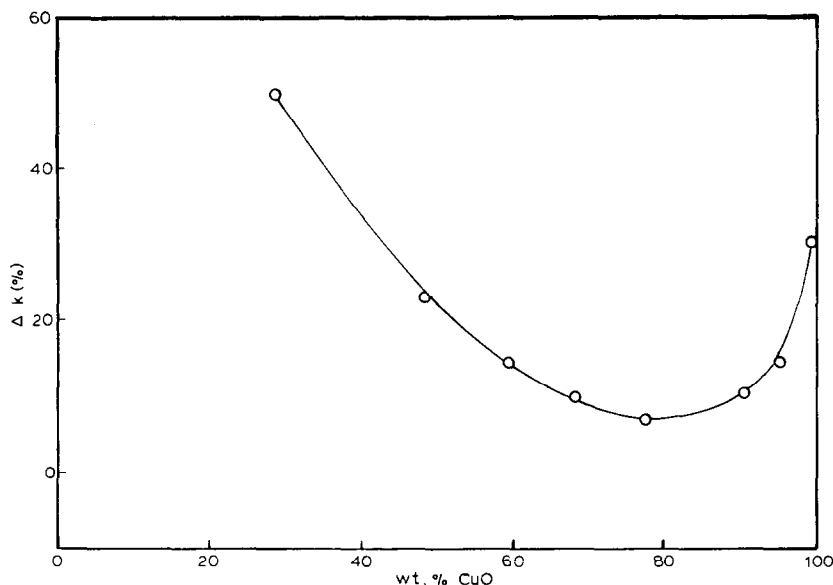


Fig. 8. Effect of γ pre-irradiation on the reduction rate of the samples of various composition. Reduction temperature, 290°C ; dose, 2.57×10^6 Gy.

comparable samples of the nitrate series, the degree of mutual interaction of the two components is lowered by the primary reduction, hence a practically mechanical mixture of the two oxides is formed by oxidation [3]. During the secondary reduction not only all the copper oxide formed is reduced, but also the other portions present in the initial samples, which were not reduced in the primary process. Their quantity increases with increasing content of Cr_2O_3 and analogously increases the degree of secondary reduction.

The influence of γ pre-irradiation on the reduction kinetics of the mixed oxides studied is shown in Fig. 8 as the dependence of the quantity Δk on the composition. This quantity is defined by the relation

$$\Delta k(\%) = 100(k^+ - k)/k,$$

where k^+ is the reduction rate constant of the irradiated sample and k is the corresponding quantity for the initial sample. The rate constants were calculated from the modified Prout-Tompkins equation, describing quantitatively the reduction kinetics of $\text{CuO-Cr}_2\text{O}_3$ mixed oxides [3] over a wide range of the degree of reduction, $\alpha = 0.05-0.9$. From the figure it is obvious that the prior irradiation leads to a positive effect (acceleration of the reduction) whose magnitude lies outside the limits of experimental errors ($\pm 8\%$) and changes markedly depending on the composition.

The relatively high value of the threshold dose of the radiation effect ($D_\gamma = 2.57 \times 10^6$ Gy) is comparable with those for pure copper oxide of various origins. The highest sensitivity towards γ radiation has been found

for the sample of carbonate origin [4]. The observed positive effect can be attributed to the non-equilibrium electrons which are captured and stabilized on the biographic lattice defects. Owing to the higher concentration of the free delocalized electrons under the reduction conditions, the reactivity of the interface increases and the crystallochemical transformation of the solid is accelerated. With decreasing free copper oxide content, the magnitude of the positive effect decreases to a minimum. With the formation of new phases in the mixed system the effect again increases.

In contrast with the initial samples, no weight loss was observed with the pre-irradiated oxides containing a high excess of Cr_2O_3 (samples No. 17–19). In this case the total radiolytic decomposition of all forms of water present, catalysed by the solid phase, can be assumed, so that the dehydration effects connected with the weight losses during the reduction (treatment in the hydrogen) of the initial samples are completely eliminated.

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