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Moderate-Temperature Reduction of Copper Chromite by Hydrogen and Hydrogen Desorption from the Surface of Reduced Chromite

A. V. Khasin, I. I. Simentsova, and T. M. Yur'eva

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—The reduction of copper chromite $CuCr_2O_4$ by hydrogen at 300–573 K and a hydrogen pressure of 4×10^4–8×10^4 Pa and hydrogen desorption from the surface of a reduced sample are studied. The rate of copper chromite reduction becomes high at temperatures above 473 K. Hydrogen desorbs from the surface of metallic copper covering the surface of chromite during its reduction. The heat of hydrogen adsorption on the metallic copper is almost independent of the surface coverage, 70–80 kJ/mol.

INTRODUCTION

It has been shown previously by structural methods that the reduction of copper chromite $CuCr_2O_4$ by hydrogen in a temperature range of 453–643 K does not result in the destruction of spinel and occurs via the redox substitution of Cu(II) atoms for hydrogen in the chromite to form reduced (metal) Cu^0 atoms on the surface of spinel. Copper(I) atoms move into the octahedral interstices. Protons substitute Cu(II) atoms in the tetrahedral interstices [1–3]. Simultaneously, hydrogen dissolves in copper chromite and neutral hydrogen atoms are incorporated into the octahedral interstices of chromite. The latter process is not accompanied by a change in the valence state of copper.

During these processes, the spinel structure of chromite is retained with minor changes. The reduction of Cu(II) to Cu^0 plays a decisive role in the interaction between hydrogen and copper chromite. Because of reduction, nearly 60% of Cu(II) atoms of copper chromite transform to metallic copper that forms flat particles epitaxially bound to the surface of spinel. Because of moderate-temperature reduction by hydrogen, copper chromite acquires catalytic activity toward acetone hydrogenation to form isopropyl alcohol [1, 3].

In this connection, it is of interest to study the interaction between hydrogen and copper chromite at moderate temperatures by kinetic and adsorption methods to probe the formation and the chemisorption properties of the active reduced chromite surface. In our previous studies, the interaction between H_2 and copper chromite $CuCr_2O_4$ was studied at low hydrogen pressures (mainly 0.1–15 Pa) when only the surface and several subsurface layers of chromite were reduced [4, 5]. The surface reduction of copper chromite was found to be an autocatalytic process indicating the intermediate stage of the dissociative adsorption of H_2 on Cu(I) or Cu^0. Hydrogen can reduce copper chromite via two pathways: (1) with the participation of subsurface and water formation and (2) without participation of oxygen through redox substitution of copper for hydrogen in the chromite mentioned above. Surface reduction occurs through both pathways, whereas subsequent reduction in the bilk occurs mainly via the second pathway [5].

In this work, we studied the reduction of copper chromite at higher hydrogen pressures, 4×10^4–8×10^4 Pa. Under these conditions, the high degrees of reduction were achieved, which are comparable with those obtained in the structural studies [1–3]. The adsorptive properties of the reduced chromite surface were studied in the experiments on hydrogen desorption.

EXPERIMENTAL

As described previously [1–5], $CuCr_2O_4$ was prepared by the thermal decomposition of copper–chromium hydroxocarbonate in air at 1173 K. Its specific surface area was 3.3 m^2/g. The sizes of grains in the samples were 0.25–0.50 mm. The study was carried out by the static volume method in a vacuum in the range from room temperature to 573 K. Interaction between H_2 and copper chromite occurred at a hydrogen pressure of 4×10^4–8×10^4 Pa along with gas circulation, which was maintained with a glass plunger pump. The gas pressure was measured with a mercury U-shaped gauge and the McLeod gauge. To protect the sample from the mercury vapor and water formed, a trap cooled with liquid nitrogen was used. The relative error in the estimation of experimental parameters was at most 1–5%.

The results of two series of runs are discussed in the paper. In each series, fresh samples (5 g) of copper chromite were used. In the first series, a sample of chromite was preheated in a vacuum at 573 K. In the second series, a sample was successively heated in a

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vacuum and treated with oxygen at a pressure of 110–140 Pa and a temperature of 573 K. Notably, the amount of oxygen thus chemisorbed did not exceed a monolayer coverage and did not considerably affect the bulk reduction of chromite. Therefore, in spite of the different preliminary treatments of samples, the results of both series have no substantial difference.

RESULTS AND DISCUSSION

Figure 1 presents the degree of copper chromite reduction y, expressed as the number of H_2 molecules consumed by one atom of Cu(II), as a function of time for the first series. Interaction between hydrogen and copper chromite was studied in the regime of stepwise temperature increase from room temperature to 573 K. The hydrogen pressure decreased because of the reaction from 8.1×10^4 to 3.7×10^4 Pa. The y value was determined by the formula

$$y = N_{H_2}M/N_A, \qquad (1)$$

where $N_{H_2} = (P_0 - P)C/g$; M is the molecular weight of copper chromite equal to 231.5; N_A is the Avogadro number; N_{H_2} is the number of reacted molecules of hydrogen per unit weight of chromite; P_0 and P are the initial and current pressures of hydrogen, respectively; C is the coefficient equal to the number of hydrogen molecules in the reaction space at unit pressure; and g is the weight of the chromite sample.

As mentioned above, it follows from the structural studies [2] that, during the interaction between hydrogen and copper chromite, Cu(II) reduces to Cu^0 and Cu(I) and hydrogen dissolves in the solid. The adsorption of hydrogen on the surface of chromite is also possible. Therefore, the y values, which characterize the total amount of hydrogen reacted, should exceed the degrees of Cu(II) reduction to Cu^0 (designated as y_1) determined in the structural studies [2]. It will be shown below (Table 1) that this excess is not high and the main fraction of hydrogen that interacts with copper chromite is consumed during the reduction of Cu(II) to Cu^0. On this basis, we can assume that the y value is the degree of reduction of chromite.

As can be seen from Fig. 1, the reaction of hydrogen with copper chromite is slow at temperatures below 473 K: the degree of reduction is only equal to 0.035 in 2 h. The surface layers of chromite are reduced and the process, as shown previously [5], occurs through both pathways described above. The reaction rate sharply increases above 473 K, and the degree of reduction at the temperatures of 523–573 K achieves ~0.65 at the same time. The bulk reduction occurs mainly via the second pathway, that is, via the redox substitution of copper for hydrogen in chromite without the participation of the chromite oxygen and water formation. Notably, the experimental data agree with those obtained by X-ray diffraction [1]. It was found in [1] that, when copper chromite is reduced by hydrogen at temperatures below ~473 K, the copper metal phase is not formed, but it appears progressively with increasing temperature. So the degree of reduction is ~50% at 593 K.

In our experiment, the temperature was decreased to room temperature after achieving $y \approx 0.65$. Figure 1 shows that the reduction process gradually decelerates at 573 K. One could expect that a decrease in temperature would cause only a further decrease in the reduction rate. The fast additional consumption of hydrogen observed after the start of sample cooling can only be explained by a reversible hydrogen adsorption whose equilibrium shifts to higher coverages (up to 1) with a decrease in the temperature. After evacuation of hydrogen at room temperature for 5 min, we carried out a run on the thermal desorption of hydrogen. The results presented in Fig. 2 show that an increase in temperature from 293 to 573 K is accompanied by the fast desorption of a significant amount of hydrogen. As a result, the hydrogen pressure increases to 3×10^3 Pa and then starts to decrease at a constant temperature of 573 K because of further interaction with copper chromite. As follows from Fig. 1, interaction between hydrogen and copper chromite continued and had a high rate when we started to cool the sample. The amount of hydrogen evolved due to desorption was equal to ~ 1.1×10^{20} molecules per 1 g of the sample. The amount of hydrogen evolved in the next run after evacuation of hydrogen desorbed was ~10 times lower. This indicates the complete desorption of surface hydrogen under these conditions. The high degree of desorption with increasing temperature to 573 K was also observed in the second series at other degrees of chromite reduction.

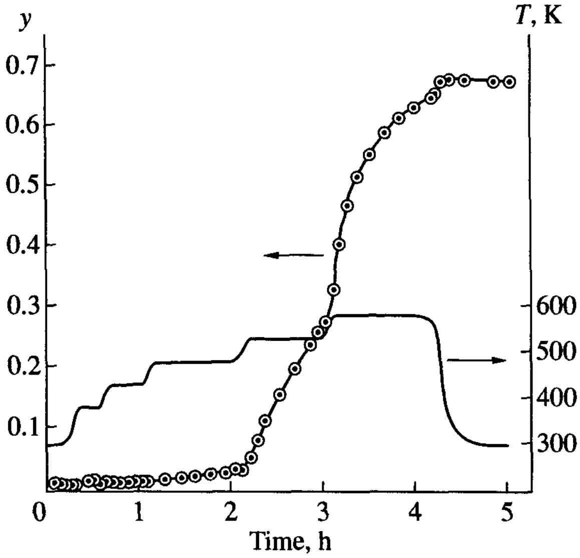

Fig. 1. The degree of copper chromite reduction as a function of interaction time during a stepwise increase in temperature from 293 to 573 K.

Table 1. Results of experiments on the reduction of copper chromite and hydrogen desorption

t, h	$N_{H_2} \times 10^{-20}$, molecule/g	y	y_1	$N \times 10^{-20}$, molecule/g	S, m^2/g	S_{Cu}, m^2/g Cu
0.3	13.8	0.53	–	1.70	19.0	–
1.0*	17.7	0.68	0.4	1.10	12.0	109
3.3	20.0	0.77	0.4	0.38	4.3	39
7.3	22.0	0.85	0.6	0.24	2.7	16
9.3	23.0	0.88	0.6	0.25	2.8	17

* The values presented in this row refer to the first series of runs and the other values refer to the second series.

On the basis of the above experimental data and the data from structural studies [1–3], it is most reasonable to assume that desorption occurs on the surface of metallic copper formed upon the reduction of copper chromite. The surface area of copper can be evaluated from the amount of hydrogen desorbed, assuming that the monolayer of adsorbed hydrogen is formed on the surface of copper after cooling the sample to room temperature in hydrogen. The chemisorption of hydrogen on copper is dissociative [6]. Therefore, the number of atoms in the adsorbed hydrogen monolayer should be equal to the number of metal atoms on the copper surface. The latter can be considered equal to 1.78×10^{19} atom/m^2 as on the Cu(111) surface. Consequently, the amount of desorbed hydrogen determined in this run, $N = 1.1 \times 10^{20}$ molecule/g, corresponds to the surface area of metallic copper

$$S = 2N/1.78 \times 10^{19} = 12 \text{ m}^2\text{/g chromite.} \quad (2)$$

The specific surface area of copper that corresponds to this value is equal to

$$S_{Cu} = (S/y_1) \times (231.5/63.5) = 109 \text{ m}^2\text{/g Cu.} \quad (3)$$

The y_1 value is the degree of Cu(II) reduction to Cu^0 equal to 0.4 according to X-ray diffraction studies [2]; 231.5 is the molecular weight of copper chromite, and 63.5 is the atomic weight of copper.

According to the electron microscopic data [1], when copper chromite is reduced under conditions close to ours, metallic copper forms plane particles with a size of 50 × 100 × 100 Å closely adjoining spinel faces, and the specific surface area of copper is equal to

$$S_{Cu} = 3 \times 10^{-16}/(8.96 \times 10^6 \times 5 \times 10^{-25}) = 67 \text{ m}^2\text{/g Cu.} \quad (4)$$

Here, 3×10^{-16} is the surface area of one copper particle available for adsorption, m^2; 8.96×10^6 is the density of copper, g/m^3; 5×10^{-25} is the volume of one copper particle, m^3.

Taking into account that this estimation is imprecise, an agreement between the values of the specific surface area of copper found by various methods can be considered satisfactory.

The second series of studies included several successive experimental runs on the alternating reduction of chromite and hydrogen desorption. In these experiments, the overall duration of copper chromite sample storage in a hydrogen atmosphere at 473–573 K gradually increased, and the degree of chromite reduction also increased. The results of the study of both series are presented in Table 1.

The t value is a duration of chromite storage in a hydrogen atmosphere at 573 K, N_{H_2} is the amount of reacted hydrogen per unit weight of chromite, y is the number of reacted hydrogen molecules per one Cu(II) atom of chromite, y_1 is the degree of Cu(II) reduction to Cu^0, N is the amount of desorbed hydrogen per unit

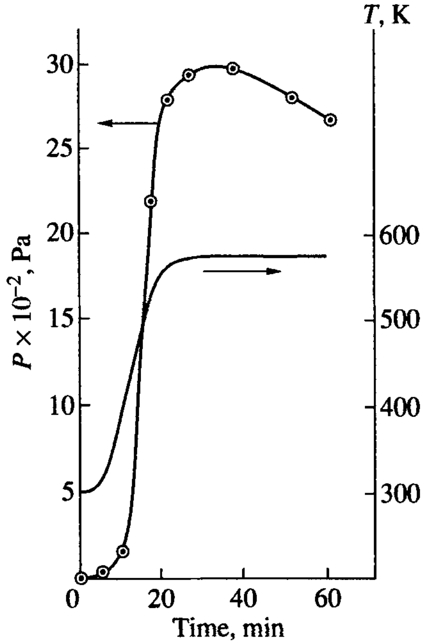

Fig. 2. Temporal profile of the hydrogen pressure in the course of thermal desorption from the sample of copper chromite reduced to $y = 0.68$ during a continuous increase in temperature to 573 K.

weight of chromite, S is the surface of metallic copper per unit weight of chromite, and S_{Cu} is the specific surface area of metallic copper. The degrees of Cu(II) reduction to Cu^0 (y_1) were estimated from the structural data for the reduction of copper chromite by hydrogen [2].

As can be seen from Table 1, the y and y_1 values differ by a factor of about 1.5. Hence, the main fraction of hydrogen is consumed for the reduction of Cu(II) in chromite to metallic copper, and a smaller fraction of hydrogen is consumed for the reduction of Cu(II) to Cu(I), dissolution in the bulk of chromite, and adsorption on the surface of reduced chromite. The amount of desorbed hydrogen decreases with increasing the contact time of hydrogen with copper chromite and the degree of chromite reduction. This can be rationalized by a decrease in the surface of metallic copper due to the growth of its particles with an increasing degree of chromite reduction. The authors of [1] found that, during reduction, flat copper particles are formed on the surface of chromite. One can assume that, as the contact time between hydrogen and copper chromite and the degree of its reduction increase, copper particles on the surface of spinel merge and form flat regions of a greater size. The surface area of the side faces of metallic particles decreases, and the surface areas of metal and spinel become closer. As seen in Table 1, at the values $y = 0.8–0.9$, the surface of metallic copper per unit weight of chromite is, in fact, close to the specific surface area of chromite, which is equal to 3.3. m^2/g.

The nature of hydrogen adsorption on the surface of reduced copper chromite can be deduced from experiments on hydrogen desorption under the stepwise heating of the sample. Figure 3 shows the results of such an experiment carried out at the degree of copper chromite reduction that corresponds to $y = 0.88$. It is seen that the adsorption equilibrium is achieved at 473 and 523 K. One can suggest that at 373 and 423 K, the system also approaches the adsorption equilibrium over the periods mentioned in Fig. 3. When the temperature is decreased to room temperature and then returned to the temperatures mentioned above, equilibration is completely reproduced at these temperatures. At the highest temperature, 573 K, the equilibrium is not achieved because of the reaction between hydrogen and copper chromite. A sequence of the states of an adsorption system, which are equilibrium and close to equilibrium, can be described by the approximate Nernst equation in the following form written for dissociative adsorption [7]:

$$\log P = -q/4.57T + 1.75\log T + i' + 2\log(\theta/1 - \theta), \qquad (5)$$

where P is the gas pressure, atm; T is the absolute temperature; i' is a conditional chemical constant (for H_2 $i' = 1.6$ [8]); q is the heat of adsorption, cal/mol; and θ is the coverage by an adsorbed substance. The heats of hydrogen adsorption were calculated according to this equation, which correspond to the coverages achieved after desorption. They were determined from the amount of hydrogen desorbed assuming as before that (1) the coverage by hydrogen at room temperature before desorption is close to unity; (2) most of the adsorbed hydrogen desorbs during heating to 573 K, and (3) the coverage at this temperature is close to zero. The experimental heats of adsorption and the values calculated according to equation (5) are presented in Table 2.

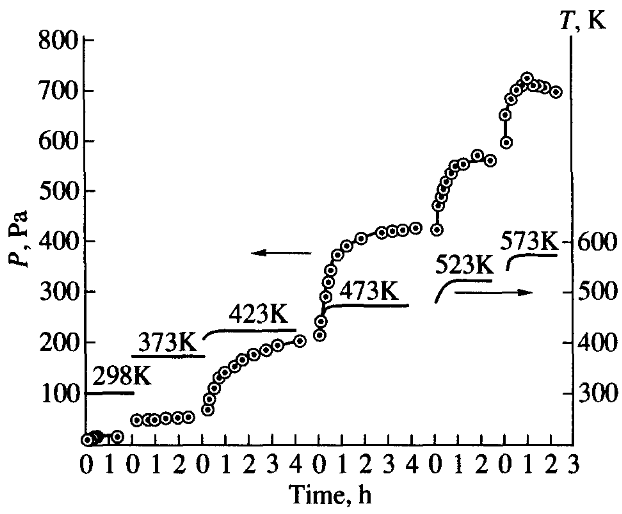

Fig. 3. Hydrogen desorption at the degree of copper chromite reduction that corresponds to $y = 0.88$: dependence of hydrogen pressure during a stepwise increase in temperature from 273 to 573 K on time.

The q values seem to be too high at 373 and 423 K, because the complete equilibrium during desorption at these temperatures was not achieved and the experimental values of P and θ used in the calculation were approximate.

The above analysis suggests that the surface of copper chromite reduced at average temperatures consists of the particles of metallic copper, and the heat of hydrogen dissociative adsorption is almost independent of coverages, 70–80 kJ/mol. The fact that this value is higher than that found for pure copper films (40–50 kJ/mol [6]) provides evidence that the chromite surface where the copper phase is formed as a layer of fine particles (50 Å) epitaxially bound to the crystal lattice of spinel affects the properties of the copper metal. The catalytic properties of this system in hydrogenation reactions can depend on the features of the chemisorp-

Table 2. Data on the adsorption equilibrium of hydrogen and the heats of hydrogen adsorption on the surface of reduced copper chromite ($y = 0.88$)

T, K	P, Pa	θ	q, kJ/mol
373	60	0.9	80
423	210	0.7	78
473	430	0.4	75
523	560	0.2	74

tion behavior of copper in the reduced copper chromite with respect to hydrogen.

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