CHEMISTRY

V. F. BALAKIREV

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

V. F. BALAKIREV

MECHANISM AND KINETICS OF THE REDUCTION OF COBALT OXIDES

(Presented by Academician G. V. Kurdyumov, 29 VI 1960)

The mechanism of the reduction of cobalt oxides is considered in works (^{1}, ^{2}). The results of these investigations, based on kinetic data, are not free from certain contradictions. Thus, some authors (^{1}) believe that Co_3O_4 is reduced in two stages: Co_3O_4–CoO and CoO–Co. Others, however, consider (^{2}) that such a course of the process is observed at temperatures above 300°, whereas at lower temperatures the CoO phase, in their opinion, is unstable and therefore does not accumulate in the reduction products.

In the present work the kinetics of the reduction of cobaltic oxide–cobaltous oxide by hydrogen was investigated, and X-ray studies of the solid reduction products were carried out. On the basis of the data obtained, the crystal-chemical mechanism of reduction is discussed. X-ray studies of the starting materials and the solid reduction products were carried out by the Debye method in a chamber 57.3 mm in diameter. The photographs were taken in Fe K_α radiation using an Mn filter, which was placed directly in the collimator of the camera. The method of loading the film was asymmetric. To determine the parameter of the crystal lattices, graphical extrapolation according to Bradley and Jay (^{3}) was used.

As the starting material, cobalt oxide Co_2O_3 of chemically pure grade was taken; X-ray structural analysis showed that it has a spinel structure and a high grain dispersion, causing blurring of the diffraction lines. To obtain cobaltic oxide –cobaltous oxide, the starting oxide was calcined at 800° for 70 h in an air atmosphere, followed by ten-hour cooling to room temperature.

The Co_3O_4 obtained proved to be single-phase, having a spinel structure with a crystal-lattice parameter in agreement with the literature data (^{4}). The sharp lines of the X-ray pattern indicated a significant increase in grain size during calcination. The oxygen content in Co_3O_4, determined from the change in weight upon complete reduction, was close to the stoichiometric value.

Reduction was carried out in a vacuum apparatus with gas circulation and freezing out of the reaction products—water vapor—in a trap cooled with liquid nitrogen (^{5}). The rate of the process was determined from the decrease in the pressure of hydrogen in the closed system over a definite interval of time.

Fig. 1. Rate of reduction of Co_3O_4 by hydrogen at a pressure of 400 mm and different temperatures

Figure 1: Fig. 1. Rate of reduction of Co_3O_4 by hydrogen at a pressure of 400 mm and different temperatures

Fig. 2. Rate of reduction of Co_3O_4 by hydrogen at 250° and different pressures

Figure 2: Fig. 2. Rate of reduction of Co_3O_4 by hydrogen at 250° and different pressures

Hydrogen was systematically added to the reaction system so that fluctuations in its pressure did not exceed $±$5–7% of the initial pressure. Experiments showed that the indicated pressure fluctuations do not have a substantial effect on the reaction rate.

The temperature was measured with a chromel–alumel thermocouple, the hot junction of which was placed directly above the sample, and the cold junction in a Dewar vessel with melting ice. The emf of the thermocouple was measured potentiomet-

type furnace. Deviations from the specified temperature during the experiment were within the limits of error of the readings of this potentiometer. Similar temperature stabilization was provided by an electronic automatic potentiometer of the EPV-01 type with a chromel–alumel thermocouple as the sensor.

After the specified temperature had been reached in the reaction space, a quartz boat with a weighed portion of 0.5 g of cobalt monoxide-oxide was introduced into the furnace by means of an electromagnet. Reduction was carried out at temperatures of 225, 250, 275, 300, 325, 350° and hydrogen pressures of 100, 200, 400, 600 mm Hg. The experimental results are presented in Figs. 1 and 2, where the process of reduction is plotted along the abscissa, and along the ordinate —the reaction rate, expressed in grams of oxygen removed from the oxide in 1 min.

Fig. 1. Rate of reduction of Co_3O_4 by hydrogen at a pressure of 400 mm and different temperatures

Fig. 2. Rate of reduction of Co_3O_4 by hydrogen at 250° and different pressures

The presence of a maximum on the kinetic curves indicates that this process develops according to the laws of topochemical reactions. The apparent activation energy of the process of reduction of Co_3O_4 by hydrogen, calculated from the temperature dependence of the reaction rate for 40% reduction from the graph in Fig. 3, is 18.5 kcal/mole.

The considerable size of the grains of the oxide being reduced determines the multizonal character of the process, which is confirmed by the smooth course of the kinetic curves and by the data of X-ray structural phase analysis, to which

Fig. 3. Dependence of $\lg K \cdot 10^3$ on T^{-1}

Figure 3: Fig. 3. Dependence of $\lg K \cdot 10^3$ on T^{-1}

samples obtained at 250° with reduction to 13.1, 21.6, 55.5, and 68.9% were subjected. Analysis of these samples showed the presence in each of them of three phases: Co_3O_4, CoO, Co, which agrees with the principle of the sequence of transformations (6).

Consequently, it may be considered that the process proceeded simultaneously on two reaction surfaces: Co_3O_4—CoO and CoO—Co. The parameter of the crystal lattice of the resulting monoxide phase CoO was 4.270 ± 0.002 Å and did not change with the degree of reduction. According to the literature data (7–10), the value of the crystal-lattice parameter

the CoO lattice varies within considerable limits, 4.22–4.32 Å. This is evidently connected with the different composition of the cobaltous oxide studied, owing to its ability to oxidize even at room temperature (11) up to $CoO_{1.10-1.15}$ (12).

The presence of cobaltous oxide in the solid products of incomplete reduction of Co_3O_4 indicates the occurrence of volume diffusion of cobalt ions in the spinel lattice of the initial phase; for its rearrangement into the NaCl-type lattice characteristic of CoO, the introduction at first of a certain number of metal ions is necessary. The spinel lattice and the NaCl-type lattice have the same arrangement of oxygen ions, which in both cases form closest cubic packings. The metal ions in spinel occupy one half of the octahedral and one eighth of the tetrahedral sites. This means that for one oxygen ion in spinel there are on average 1/2 metal ion in octahedral sites and 1/4 metal ion in tetrahedral sites. In CoO of stoichiometric composition all octahedral sites are filled by metal ions, while all tetrahedral sites are vacant. As a result, for one oxygen ion in the CoO crystal lattice there is one cobalt ion in octahedral sites.

During the Co_3O_4—CoO transformation, cobalt ions pass from tetrahedral sites into octahedral ones. But this is still insufficient for complete transformation, since in this case only 3/4 of the octahedral sites of the crystal lattice of stoichiometric CoO composition would be filled. The remaining vacant fourth part of the octahedral sites is filled by metal ions appearing on the surface of the oxide as a result of its reduction, only by volume diffusion.

Fig. 3. Dependence of $\lg K \cdot 10^3$ on T^{-1}

On the basis of the experimental data and crystal-chemical concepts set forth above, the following mechanism may be proposed for the reduction of cobaltous-cobaltic oxide to cobaltous oxide. During reduction, as a result of the removal of oxygen by hydrogen on the surface of the crystals, ions of metallic cobalt are liberated; under the action of the concentration gradient, part of them diffuse into the lattice of the initial phase, causing the transformation of Co_3O_4 into CoO. The CoO crystals formed at the first moment must have the maximum number of vacancies, which are filled by cobalt ions arriving from the surface. The latter, diffusing through the CoO lattice, penetrate into the lattice of the initial Co_3O_4, causing its further transformation into CoO.

However, volume diffusion at the relatively low temperatures at which the experiments were carried out proceeds comparatively slowly, while the rate of the chemical reaction at the gas-solid surface, which supplies the metal ions, is high. Therefore, part of the metal ions liberated on the oxide surface during its reduction does not have time to penetrate into the crystals and forms a metallic phase much earlier than all the Co_3O_4 is transformed into CoO.

The constant presence on the surface of an excess of cobalt ions leads to the fact that, throughout the entire process, the CoO phase proves to be maximally saturated with metal; therefore the parameter of its crystal lattice remains unchanged irrespective of the degree of reduction. The lattice parameter of such cobaltous oxide was determined to be 4.270 ± 0.002 Å.

Further growth of the metal crystals occurs by diffusion of cobalt ions along the metal-oxide interface and along the free surface of the crystals.

The author expresses gratitude to the supervisor of the work, Corresponding Member of the Academy of Sciences of the USSR G. I. Chufarov, for the assistance rendered in carrying it out.

Institute of Metallurgy
Ural Branch of the Academy of Sciences of the USSR

Received
27 VI 1960

REFERENCES

1. G. I. Chufarov, M. G. Zhuravleva, E. P. Tatievskaya, DAN, **73**, No. 6, 1209 (1950).
2. A. N. Kuznetsov, A. A. Shestopalov, N. F. Kulish, ZhFKh, **32**, No. 1, 73 (1958).
3. A. J. Bradley, A. H. Jay, Proc. Phys. Soc., **44**, 563 (1932).
4. B. F. Ormont, *Structures of Inorganic Substances*, L., 1950, p. 629.
5. E. P. Tatievskaya, G. I. Chufarov, Izv. AN SSSR, OTN, No. 7, 1035 (1946).
6. A. A. Baikov, *Metallurg*, No. 3, 5 (1926).
7. B. G. Lebedev, in: *Collected Works. Moscow Institute of Steel named after I. V. Stalin*, M., 1938, p. 178.

8. I. A. Arkharov, K. M. Graevskii, ZhTF, **14**, No. 3, 132 (1944).
9. Schenck, Wisselkock, Zs. anorg. u. allgem. Chem., **184**, 39 (1929).
10. S. Holgersson, A. Karlsson, Zs. anorg. u. allgem. Chem., **182**, 255 (1929).
11. M. LeBlank, E. Möbius, Zs. phys. Chem., **A142**, 162 (1929).
12. C. B. Holtermann, Ann. Chim., **14**, 121 (1940).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.