Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

Zh. P. KACHANOVA, Corresponding Member of the Academy of Sciences of the USSR V. V. VOEVODSKII, and A. P. PURMAL

1960

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196001.50403

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

SovietRxiv

Fig. 1. Scheme for measuring the electrical conductivity of MnO_2

Figure 1: Fig. 1. Scheme for measuring the electrical conductivity of MnO_2

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Vol. 135, No. 3

PHYSICAL CHEMISTRY

Zh. P. KACHANOVA, Corresponding Member of the Academy of Sciences of the USSR V. V. VOEVODSKII, and A. P. PURMAL

ELECTRICAL CONDUCTIVITY OF THE SEMICONDUCTOR MnO_2 DURING THE CO OXIDATION REACTION

According to ideas developed in recent years, there exists a definite correlation between the catalytic and electronic properties of semiconductor catalysts ($^{1-13}$). In most works, the catalytic activity of samples is compared with their electronic properties, regulated by changing the stoichiometry or by introducing impurities. Considerably less attention is paid to the study of changes in the electronic properties of semiconductor catalysts during the catalytic process itself. Among researchers concerned with questions of semiconductor catalysis, there is at present no consensus as to whether the reaction process itself should cause reversible changes in the electronic properties of the catalyst.

Fig. 1. Scheme for measuring the electrical conductivity of MnO_2

According to the general ideas developed by one of the authors (^{14}), the course of a catalytic process should be accompanied by reversible excitation of the catalyst under the influence of the catalytic process itself. A significant increase in electrical conductivity during the catalytic process was observed in the work of Polish authors (^{9}). However, this effect is associated with macrochemical transformations of the samples. An increase in the electrical conductivity of the catalyst (film CuO) under conditions excluding the influence of side factors was observed during the reaction by Lyashenko and Stepko (^{12,13}). The aim of our work was the quantitative study of similar effects.

MnO_2—a CO oxidation catalyst that does not undergo macrochemical changes in the working temperature range (60–140°)—was selected as the object of investigation. The experiments were carried out in a vacuum flow-circulation ap-

SovietRxiv

Fig. 2

Figure 2: Fig. 2

paratus with freezing out of CO_2 and automatic regulation of the constancy of pressure in the system. The catalyst sample was a pellet pressed from electrolytic, finely dispersed MnO_2 with a specific surface area of 150 m^2/g ($P = 2.5$ t/cm^2, $d = 9$ mm, $l = 13$ mm). The temperature was measured with a chromel–alumel thermocouple pressed to the surface of the pellet by a Teflon holder. Four gold contacts for measuring electrical conductivity were fastened in the same way. Measurements were carried out according to two circuits (Fig. 1) and gave the quantities R_{own} and $R_{\text{Au}-\text{MnO}_2}$—the resistance of the near-contact layer. In the course of the work it was established that $R_{\text{Au}-\text{MnO}_2}$ does not change during the reaction or upon adsorption of the components. Measurements of the Hall effect and of the thermoelectromotive force showed that MnO_2 is an n-semiconductor*. The specific resistance of the sample varied within the limits 0.8–$2.2 \cdot 10^3$ $\Omega \cdot \text{cm}$.

* The measurements were carried out by T. I. Kolomenskaya at the Physics Institute of the Academy of Sciences of the USSR.

In the process of conditioning the sample, two stages can be distinguished. At first the catalytic activity of the sample is low, but it increases from run to run. No differences are observed between the electrical conductivity of the sample conducting the reaction and that of the sample in vacuum. The only noteworthy fact is that already in this regime the oxygen present in the reaction mixture does not change the electrical conductivity of the sample during the reaction, whereas adsorption of O_2 significantly decreases the conductivity of the sample. This fact can be explained either by the absence of adsorbed oxygen (adsorption of CO and CO_2 does not change the electrical conductivity as compared with vacuum), or by compensation, at all pressures and temperatures, of the decrease in conductivity due to oxygen by its increase under the influence of the reaction. The latter seems unlikely. The second stage is characterized by constant catalytic activity of the sample under standard-treatment conditions: half-hour heating in an O_2 atmosphere and half-hour evacuation at 200°. Characteristic changes in electrical conductivity under the influence of adsorption of O_2, CO, CO_2, and of the reaction are shown in Fig. 2. As is seen from the data presented in Fig. 2, the electrical conductivity during the reaction greatly exceeds the electrical conductivity of the sample in vacuum. This change in σ is reversible, appearing when the reaction mixture is introduced and disappearing completely upon its rapid evacuation. Under the influence of oxygen the electrical conductivity decreases considerably, while upon adsorption of CO it increases only very slightly.

Fig. 2. Temperature dependence of the electrical conductivity of MnO_2. *a*—in oxygen, *b*—in vacuum, *v*—in carbon monoxide, *g*—in carbon dioxide, *d*—in the reaction. A stoichiometric mixture was taken: 1—10 mm, 2—20 mm, 3—45 mm,

SovietRxiv

Fig. 3

Figure 3: Fig. 3

4—85 mm.

The activation energy of the electrical conductivity of the sample during the reaction did not change as compared with the conditions in vacuum and was equal (for different series) to 2-3 kcal/mole. This shows that during the reaction no new levels are created, but only the effective population of the upper level already existing in vacuum increases.

Fig. 3. Dependence of the increase in the electrical conductivity of MnO_2 compared with the electrical conductivity in vacuum on the reaction rate at different temperatures.

Figure 3 shows the dependences $\Delta\sigma$—w (rate in arbitrary units) at different temperatures and the temperature dependence of the quantity $w/\Delta\sigma$ ($\Delta\sigma$ is the increase in electrical conductivity during the reaction as compared with the electrical conductivity in vacuum). The quantity $\Delta\sigma/w$ is a characteristic of the deviation of the catalyst from the thermodynamic equilibrium state under the influence of the reaction. With increasing temperature, i.e., with increasing rate of the energy-dissipation processes leading to the establishment of thermodynamic equilibrium, the quantity $\Delta\sigma/w$ decreases regularly. A linear dependence between $\Delta\sigma$ and w was observed during reactions with mixtures of the following composition: from 30% to 80% CO; moreover, with an increase in the percentage oxygen content in the mixture, the quantity $\Delta\sigma/w$ decreased, which also lim-

made possible the measurement of $\Delta\sigma$ in mixtures strongly diluted with oxygen. The decrease in $\Delta\sigma/w$ in experiments with a high oxygen content is not connected with its adsorption, since extrapolation of the straight line σ—w leads σ to σ_{vac} at $w = 0$, whereas a noticeable decrease in the electrical conductivity under the influence of O_2 begins already at a pressure of several hundredths of a millimeter of mercury and reaches saturation at 0.1—1 mm. For mixtures richer in CO, the dependence between w and $\Delta\sigma$ assumes a complex character.

Thus, as a result of the work carried out it has been established that in the course of the catalytic process ($CO + O_2$) the catalyst-semiconductor (MnO_2) is in a state of electronic excitation, i.e., in a thermodynamically nonequilibrium state. A correlation between the rate of the process and the degree of nonequilibrium of the catalyst was found under all investigated conditions. In the course of the CO oxidation reaction on MnO_2, adsorption of oxygen does not occur.

The authors are grateful to B. P. Bruns for kindly providing samples of electrolytic manganese dioxide.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
18 VI 1960

CITED LITERATURE

1. V. V. Voevodskii, F. F. Vol' kenshtein, N. N. Semenov, *Problems of Chemical Kinetics and Reactivity*, 1955, p. 423.
2. S. Z. Roginskii, *Problems of Kinetics and Catalysis*, **8**, 5 (1955).
3. F. F. Vol' kenshtein, *Problems of Kinetics and Catalysis*, **8**, 79 (1955).
4. F. F. Vol' kenshtein, *ZhFKh*, **23**, 917 (1949).
5. F. F. Vol' kenshtein, *ZhFKh*, **21**, 1317 (1947).
6. F. F. Vol' kenshtein, *ZhFKh*, **26**, 1962 (1952).
7. F. F. Vol' kenshtein, *ZhFKh*, **27**, 159, 167 (1953).
8. Collected volume: *Catalysis. Electronic Phenomena*, Foreign Literature Publishing House, 1959.
9. L. Belyanskii, G. Deren' , G. Gabar, *Bulletin of the Polish Academy of Sciences*, Div. 3, **3**, No. 4, 221 (1955); No. 9, 491 (1955).
10. I. A. Myanikov, S. Ya. Pshezhetskii, *Problems of Kinetics and Catalysis*, **8**, 175 (1955).
11. K. I. Matveev, G. K. Boreskov, *Problems of Kinetics and Catalysis*, **8**, 165 (1955).
12. V. I. Lyashenko, I. I. Stepanov, *Problems of Kinetics and Catalysis*, **8**, 180 (1959).
13. V. I. Lyashenko, I. I. Stepko, *ZhFKh*, **29**, 401 (1955).
14. V. V. Voevodskii, *Problems of Kinetics and Catalysis*, **8**, 97 (1955).

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

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