Heat conductivity of copper-zinc catalysts used for producing methyl alcohol

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Abstract. The paper presents the results of an experimental study of the thermal conductivity of copper-zinc catalysts in a wide range of temperature changes and various concentrations of component components, which ranged from 10 to 90%. To achieve this goal, we used a device developed on the basis of the method of monotonous heating to measure the thermal conductivity of samples depending on changes in the experimental temperature up to 400K. Based on the results obtained using the law of corresponding states, the corresponding empirical equations were derived that allow calculating the thermal conductivity of experimentally unexplored samples with an error of no more than 4%.

1. Introduction
As you know, the thermal conductivity of materials and substances is a process that is accompanied by the distribution of heat according to the results of the Coulomb (electromagnetic) interaction with a distinctive temperature of individual particles of the body under consideration, i.e. accompanied by the exchange of energy between particles of the material [1,2].
Copper-zinc catalysts are widely used in industrial and household chemicals for the production of various detergents and cleaners, in the preparation of primary fatty alcohols, in the dehydrogenation of ethyl alcohol, in the preparation of formaldehydes, in the production of methanol at significantly low temperatures, in various redox reactions, in the form of plates they are used as a galvanic cell as a chemical source of electricity (Daniel-Jacobi cell, which served as the basis for the discovery and the corresponding invention of more advanced and reliable chemical energy sources) and much more [3].
Reducing the size of materials and substances (in our case, shavings) often leads not only to a change in their properties, but also to the acquisition of completely new properties. This is due to an increase in the surface area and, accordingly, the role of surface atoms and interactions. The transition of the substance to small sizes gives rise to unique properties that can be used in the development and development of new materials and technologies. Not only physico-chemical properties, but also the reactivity of a substance in such a state will differ from its massive counterparts. This lays the foundation for creating completely new functional materials like sensors, adsorbents, membranes, fillers, as well as catalysts. As you know, about 90% of the processes of refining petroleum, chemical and petrochemical raw materials, the production of chemical materials and products are catalytic. Catalytic technologies also form the basis of most environmental technologies and even energy production. Size effects in catalysis on metals have been known since the discovery of structurally sensitive and structurally insensitive reactions by Budar.
Among other materials, metallic particles occupy a special place because of the peculiarity of their electronic structure and the simplicity of their preparation [2, 4].

The results of various studies of copper-zinc catalysts formed the basis of most modern scientific and technical discoveries of a wide range of uses, but I would like to note that their thermophysical properties have not been studied in detail, and existing theories do not allow them to be calculated with the necessary accuracy for science and practice. In this connection, the appeal to the experiment is the only correct solution to this problem. Modern methods for studying thermal processes used in the description of heat transfer processes in technically important materials and substances need a set of theoretically substantiated and practically confirmed data. In connection with this, experimental studies of the properties of substances and materials come to the fore, since the vast majority of engineering and applied problems require reliable data, and even as close as possible data on the properties of the necessary materials can lead to significant errors and shortcomings in the design and development processes new technologies and materials. In recent years, in connection with the improvement of gas purification methods and the development of engineering and technology, zinc (copper-aluminum and zinc-copper catalysts) are used. It is known that copper-containing catalysts increase the rate of formation of methanol from synthesis gas, however, they rapidly become inert due to the presence of in the synthesis gas of sulfur impurities. The use of copper-containing catalysts allows the synthesis of methanol at low temperature and pressure.

In the 1920s, when a thermodynamic study of the reaction of methanol synthesis from H2 and CO made it possible to determine the conditions under which the equilibrium state is favorable for this synthesis, the problem of methanol production from relatively cheap raw materials was solved. The results also indicated that the earlier searches for more active catalysts were not blamed for failure due to their low activity, but as a result of an insufficiently favorable equilibrium under the conditions under which they attempted to carry out this reaction [6].

The main objectives of the design and research work in the field of methanol synthesis are to increase the capacity of the columns to bring the unit capacity to 100 000 tons per year for raw methanol, increase the mechanical strength and activity of the catalysts used in the synthesis, improve these catalysts, develop new designs of nozzles for the synthesis columns, development of methods for thorough gas purification from oil and iron carbonyls. The temperature of 360 - 370 °C is considered optimal in the synthesis of methanol. However, it should be noted that maintaining such a temperature over the entire height of the column is a difficult task, since the temperature depends on the influence of many factors of the gas composition, state of the catalyst, equipment, their physicochemical properties and etc. Therefore, they usually work in the temperature range 360 ± 20 °C.

Accurate temperature control in the synthesis column is important. Temperature fluctuations lead to the development of undesirable reactions and to a deterioration in the quality of raw methanol. Methanation reactions are especially dangerous, accompanied by a sharp jump in temperature (up to 1000 °C), which causes sintering of the catalyst.

It was proved that the isothermal process is the optimal mode of methanol synthesis [1987].

The temperature and pressure at which the formation of methanol proceeds depend on the type of catalyst used, the composition of the synthesis gas. The main source of synthesis gas is natural gas conversion. The composition of the convertible gas should be characterized by a certain ratio of components (H2 + CO2) (CO2 + CO2). For the synthesis of methanol under industrial conditions, this ratio should be in the range of [6].

Based on the foregoing, we carried out a comprehensive study to study the thermophysical properties (thermal conductivity, heat capacity, thermal diffusivity) of copper-zinc catalysts in a wide range of temperature changes, the concentration of component components (copper and zinc), which varied from 10 to 90%. To achieve this goal, we used a device developed on the basis of the monotonic heating method for measuring the thermal conductivity of samples depending on changes in the experimental temperature to 400K [5].

This method finds a solution by approximate analysis of the equation of nonlinear heat conduction, despite the fact that the method implies smooth heating (cooling) of the test sample at different temperatures (from the temperature of liquid nitrogen to 673K). Such methods make it possible to
generalize quasistationary methods when the thermophysical parameters are variable. These methods are also called dynamic, because by means of one experiment it is possible to determine the temperature dependence of the test substance.

For the experimental study of heat capacity, thermal conductivity and thermal diffusivity of materials and substances, this method is used quite actively. Thanks to the changes made to the installation, i.e. the establishment of the cell made it possible to use it to measure the thermal conductivity of liquids and solutions, which could not be done in the earlier version of the measuring device.

The thermal circuit of the measuring device, the principle of operation of which is based on the method of monotonous heating, is illustrated in Figure 1. The heat flux coming from the base 1 monotonically heats the rod 5, contact plate 3, and sample 4, which in turn is placed in a copper cell. The cell along with the material being studied, contact plates, and also the rod from the lateral surfaces are adiabatically isolated.

All the main element of the device is made of copper, to a large extent, to exclude temperature differences.

![Thermal diagram of a device based on the method of monotonous heating](image)

**Figure 1.** Thermal diagram of a device based on the method of monotonous heating: 1 – base; 2 – plate; 3 – contact plate; 4 – copper cell with the test sample; 5 – core.

From the base 1, a heat flow is supplied, which, passing through the plate 2, is partially absorbed by it and then goes to the plate 3, warming it up to the cell with the prototype 4 and the rod 5. The dimensions of all parts of this circuit are selected so that the heat fluxes coming from the base, which are accumulated by the plate and the cell with the prototype, were at least 5-10 times less than which the rod absorbs.

In this scheme, all the details, due to the fact that they are made of copper, are heated at speeds close to each other, and heat fluxes \( Q_0 (\tau) \) and \( Q_T (\tau) \) at any temperature are calculated by the formula:

\[
Q_0 (\tau) = \frac{\Delta T_0 S}{P} = \left( \frac{1}{2} C_0 + C_r \right) \cdot \nu_0
\]

where \( Q_0 (\tau) \) - is the heat flux that passes through the prototype and is then absorbed by the rod, W; \( \Delta T_0 \) - temperature difference of the sample, K; P - is the thermal resistance that occurs between the
contact plate and the rod, m²K/W; C₀ - is the total heat capacity of the investigated material (substance), J/K; Cₖ - the heat capacity of the rod in general form, J/K; ν₀ is the heating rate of the measuring cell, K/s; S - area related to the cross section of the measuring cell, m².

\[ Q_T(\tau) = K_T^* \cdot v_T = \left( \frac{1}{2} C_T + C_n + C_0 + C_\kappa \right) \cdot v_0 \]  

(2)

here \( Q_T(\tau) \) - is the heat flux that passes through the plate, W; \( K_T^* \) - proportionality coefficient, which shows the effective heat conductivity of the plate, W/K; \( v_T \) - is the temperature difference of the plate 2, K; \( C_T \) - is the total heat capacity of the plate 2, J/K; \( C_\kappa \) - is the total heat capacity of the contact plate 3, J/K.

The thermal resistance that occurs between the contact plate and the rod is calculated by the formula:

\[ P = P_0 + P_K \]  

(3)

where \( P_0 \) - is the thermal resistance of the test material (substance), m²K/W; \( P_K \) - correction, which takes into account the thermal resistance of the contact and terminations of thermocouples, dissimilarity, m²K/W.

The thermal resistance of the test material (substance) is calculated by the equation:

\[ P_0 = \frac{h}{\lambda} \]  

(4)

here \( h \) - is the height of the investigated material (substance) i.e. cell height, in which the prototype is directly located, m; \( \lambda \) - thermal conductivity of the investigated material (substance), W/(m·K).

Using formulas (1) - (4), formulas were derived for calculating the thermal resistance of the studied materials (substances) and their thermal conductivity.

\[ P_0 = \frac{\Delta T_0 S(1 + \sigma_\kappa)}{\Delta T \cdot K_T} - P_K \]  

(5)

here \( \sigma_\kappa \) - is a correction that takes into account the heat capacity of the cell with the test material made of copper:

\[ \sigma_\kappa = \frac{C_0}{2(C_0 + C_\kappa)} \]  

(6)

In formula 6, the letters \( C_\kappa \) and \( C_0 \) denote the total heat capacity of the rod and the sample (test material), respectively, J/K.

\[ C_0 = C_0(t) \cdot m_0 \]  

(7)

Here the letter indicates the specific heat of the cell with the prototype, J/(kg·K); \( m_0 \) is the mass of the investigated material (substance), kg:
where is $C_M(t)$ - the specific heat of copper itself, J/(kg \cdot K); $m_c$ - is the mass of the rod, kg.

The value of $\sigma_c$ - can be selected tentatively according to the heat capacity of the material (substance) under study, since the influence of this value exceeds 5-10%.

The following relationship is used to calculate the thermal conductivity of the plate:

$$K_T = K_T^* \frac{C_c}{\frac{1}{2}C_T + C_n + C_c}$$  \hspace{1cm} (9)$$

Using the formula (4) we obtain:

$$\lambda = \frac{h}{P_0}$$  \hspace{1cm} (10)$$

The values of $C_T$ and $P_K$ are constants of the measuring device, which are established by grading using control samples (copper, kerosene, toluene, water) and do not depend on the properties of the experimental material (substance). To determine the thermal conductivity of the studied material during the experiment at different given temperatures, one should measure the temperature drop on the heat meter and the studied material (substance) $\Delta T_1$ and $\Delta T_0$, accordingly, in microvolts ($\mu$V), $n_1$ and $n_0$.

As samples, finely dispersed (shavings) copper-zinc catalysts, which are actively used in industry and in the production of methanol, were taken for research.

In the setup presented above, we carried out a number of experimental studies, one of which is the measurement of the thermal conductivity of copper-zinc catalysts depending on the change in the temperature of the experiment, and the concentration of composite components, the results of which are shown in Figure 2.

![Figure 2](image-url)  \hspace{1cm} \textbf{Figure 2.} Experimental values of the thermal conductivity of copper-zinc catalysts of different concentrations of component components at different temperatures.
As can be seen from the figure, the thermal conductivity of copper-zinc catalysts increases, depending on the decrease in the concentration of the second component, however, with a temperature increase from 250-255 °C it first increases, and then it decreases.

Many classifications of heterogeneous catalysts can be proposed depending on the properties considered. However, for the convenience of considering the influence of various factors on their catalytic properties, mainly heterogeneous catalysts are divided into two groups: metals and non-metals, for each of which corresponding theoretical approaches have been developed to explain and predict their catalytic properties.

To go into the activated state, the reagent molecule needs to go through the chemisorption stage at the active center of the catalyst. The strength of adsorption of the reagent is a determining factor in the efficiency of catalysis. Moreover, both too strong adsorption and too weak adsorption does not lead to high activity.

It is known that copper-containing catalysts allow the synthesis of methanol at significantly low temperatures and pressures and contributes to an increase in the rate of its formation, however, as already noted, it quickly goes into an inert state. The experimental data we obtained can serve as the basis for solving these problems [6].

We also performed a series of experimental studies on other concentrations of composite components, the results of which led to the corresponding empirical equations that allowed us to calculate the thermal conductivity of copper-zinc catalysts with an error of no more than 3 percent, and at individual points no more than 5%.

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