Experimental study on the structure formation features of a filler of catalytic heating systems

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Abstract. In the paper, we present an experimental study on the structure formation of a filler of catalytic heating systems. As a result, the dependences of the parameters of technological processes for the preparation of catalysts on their structure being formed were identified.

1. Introduction
The transition to nanometer-sized particles of a catalytically active substance can cause a change in the specific catalytic activity (SCA), which can be found as a ratio of the reaction rate in the presence of a catalyst to the number of surface (available) metal atoms. This indicates the appearance of a size effect in structurally sensitive catalytic reactions, the rate of which, unlike structurally insensitive reactions, varies with the change of average particle size of the active component [1].

Studying the features of structure formation (including nanostructures) of catalytic systems fillers for producing catalysts with strictly controlled properties makes it possible to obtain more active catalysts (with a given particle size) and more selective ones (with a uniform particle size distribution), thereby allowing to optimize existing processes by reducing energy consumption (temperature of the reaction) and the amount of harmful emissions, as well as increasing the yield of valuable products and, as a consequence, offer a new technological scheme for processing of petrochemical and chemical raw materials and utilization of emission of various stationary sources and transports [1].

The use of catalytic devices for heating allows increasing the performance of heating systems by improving the efficiency of the combustion process and reducing emissions of harmful gases into the atmosphere.

Also the formation of a catalytically active coating is associated with the technology of its deposition. Therefore, the identification of the features of optimal structure formation of a catalytic coating depending on the parameters of technological processes is topical.

The purpose of this paper is to experimentally investigate the relationship between the parameters of technological processes for the preparation of catalysts and their structure being formed.

2. Design and results of an experimental study on the structure formation features of a filler of catalytic systems
To create experimental samples of catalyst, two types of silica gel were taken as a basis: coarse macropored granular silica gel (KSKG) and coarse fine-pored granular silica gel (KSMG).

For the making catalysts, the co-precipitation method was used [2 - 4]. With the help of this method, it is necessary, on the surface of a carrier, which is silica gel, to obtain a film of a metal oxide having a catalytic activity to the reactions of complete oxidation of hydrocarbons.
Silica gels have a characteristic structure. The average effective pore diameter of silica gels is in the range of 20-150 Å, and the specific surface area is 102-103 m²/g. Thus, the deposition of metal oxide on the surface, which has a characteristic structure, will make it possible to create an active oxide catalyst film, which has a similar structure. It is worth noting that silica gels, as well as zeolites and quartz aerogel, which were also considered as possible carriers for active coating, are resistant to the constituents of biogas, which makes them suitable for use in catalytic heating devices operating on biogas. The deposition of the catalytically active coating was carried out in the following sequence. In the first stage we prepared solutions of alkali and metal salt. Then, these solutions were merged in the presence of a silica gel (carrier). The surface of the silica gel acted as nuclei for the formation of a solid phase of precipitation of metal hydroxide. The carrier was then removed and dried in air. After partial drying, the carrier in crucibles was placed in a muffle furnace, where it was calcined until the formation of metal oxide of a characteristic color.

When conducting experiment, copper oxide was chosen as the active catalytic coating. For this purpose, copper sulfate pentahydrate GOST-4105-78 (CuSO₄·5H₂O) and sodium hydroxide GOST-4328-77 (NaOH) were selected as reagents. The purpose of the experiment was to identify the features of the structure formation of a catalytically active coating of copper oxide at different concentrations of the initial reagents on different types of silica gel.

Thus, 3 factors for the experimental study were determined: the concentration of copper sulfate solution, the concentration of sodium hydroxide solution and silica gel type. The levels of variation of the factors were selected based on preliminary experiments to estimate the amount of metal hydroxide precipitate at various concentrations of the initial mixtures. The levels of variation are given in table 1. On the basis of the accepted levels of variation of factors, an experimental design was created (table 2).

| Level of variation | Concentration of copper sulfate solution, % | Concentration of sodium hydroxide solution, % | Silica gel type |
|--------------------|--------------------------------------------|-----------------------------------------------|----------------|
| 1                  | 1                                          | 5                                             | KSMG           |
| 2                  | 5                                          | 10                                            | KSKG           |
| 3                  | 10                                         | -                                             | -              |
| 4                  | 15                                         | -                                             | -              |

| Type of silica gel | Concentration of copper sulfate solution, % | Concentration of sodium hydroxide solution, % |
|--------------------|---------------------------------------------|-----------------------------------------------|
|                    | 1                                           | 5                                             |
|                    | 1                                           | 10                                            |
|                    | 15                                          | 10                                            |
| KSMG               | 1                                           | 5                                             |
|                    | 1                                           | 15                                            |
|                    | 15                                          | 5                                             |
|                    | 10                                          | 5                                             |
| KSKG               | 15                                          | 10                                            |
|                    | 1                                           | 5                                             |
|                    | 10                                          | 10                                            |
|                    | 15                                          | 15                                            |
To prepare solutions we used beakers with a printed scale in milliliters, as well as precision scales ‘Ohaus Adventurer Pro’. Stirring was carried out using glass rods and a mixing device manufactured by Ekros Ltd. The degree of dissolution of the reagents was checked visually, and stirring was carried out until their complete dissolution.

The obtained samples very clearly represented the effect of the concentrations of reagents on the amount of precipitated copper hydroxide on the surface of the carrier. After draining, all the samples turned blue, which indicated the presence of copper hydroxide on the surface and in the pores of silica gel, but the difference in color saturation with any of the studied factors was clearly seen. This confirms the relevance of the factors and the levels of their variation determined for the experimental design. For KSKG silica gel, only one sample was 10% of sodium hydroxide solution. This is due to the high degree of destruction of the carrier under the action of alkali of the selected concentration. Thus, further study of KSKG silica gel with a higher concentration of sodium hydroxide solution was defined as not promising. After partial drying, the samples were calcined in a muffle furnace at a temperature of 400 °C for 1 hour.

The obtained samples were examined using the NTEGRA PRIMA BASIC probe microscope. For experiments with probe microscopy [5], a simplified experimental design was created, shown in table 3. The results of experiments are presented in figure 1 – figure 3.

| Type of silica gel | Concentration of copper sulfate solution | Concentration of sodium hydroxide solution |
|--------------------|----------------------------------------|------------------------------------------|
| KSMG               | 1%                                     | 10%                                      |
|                    | 15%                                    |                                          |
| KSKG               | 1%                                     | 5%                                       |
|                    | 15%                                    |                                          |
| KSMG               | -                                      | -                                        |
| KSKG               | -                                      | -                                        |

**Table 3.** Simplified experimental design.

Figure 1 show the results of scanning samples of silica gel of types KSMG and KSKG on a scale of 4×4 microns. The three-dimensional images clearly show the complex structure of silica gels, but the surface of KSMG has a smoother surface profile than that of KSKG, which is caused by greater orderliness due to the smaller pore diameter.

Scanning results were also obtained for samples after deposition of a catalytically active coating. For KSMG with a concentration of sodium hydroxide of 10% and copper sulfate of 1% and 15%, the results are presented in figure 2. It is clearly seen that the surface of the sample obtained using a 1% copper sulfate solution is characterized by a large number of deviations from the object profile than the sample obtained using a 15% copper sulfate solution. This allows us to suggest a significant reduction in number of pores when using a more concentrated solution of copper sulfate, which is
associated with a significant deposition of the coating and clogging of the pores. The overall profile of the surfaces remains similar for both samples.

Figure 2. Results of scanning samples of KSMG with a 10% sodium hydroxide solution and 1% (top figure) and 15% (bottom figure) copper sulfate solutions.

Figure 3 shows the results of scanning for samples of KSCG silica gel with a 5% sodium hydroxide solution and 1% and 15% copper sulfate solutions. The surface profiles of the samples are different, due to the peculiarities of the choice of the scanning area. However, the magnitude of the deviations in both samples is considerable. This allows us to conclude that the surfaces of both samples are formed by a significant number of pores.

3. Conclusions
The results of the experimental study on the structure formation features of a filler of catalytic systems indicate the explicit dependence of the parameters of technological processes for the preparation of catalysts on their structure. Thus, the optimal structure of a catalytically active coating characterized
by the preservation of a significant number of carrier pores is formed on the surface of carrier, which is silica gel of type KSKG, when, for its preparation, alkali solutions of low concentration are used due to the possibility of destruction of the carrier surface by those of higher one.

Figure 3. The results of scanning samples of KSKG with a 5% sodium hydroxide solution and 1% (top figure) and 15% (bottom figure) copper sulfate solutions.

References
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