Colloidal-chemical basis for the development of perspective catalytic systems based on CeO_2-ZrO_2 and Mo_2C-W_2C

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Abstract. The sol-gel method is known for over 70 years and is currently successfully implemented to produce various materials: ceramics, composites, glasses, optical coatings, electronics, sorbents, membranes etc. The wide use of the sol-gel method is due to its advantages compared to traditional technologies.

Sol-gel method has a great potential of supported materials preparation, especially in the field of catalytic chemistry. Sol-gel method opens opportunities to synthesize perspective multicomponent supported catalysts and membrane catalysts (catalytic membranes).

At the present time in the field of catalyst preparation the most implemented technologies based on the sol-gel method is deal with several oxides: SiO_2, TiO_2, ZrO_2, and Al_2O_3. This is due not only to a wide range of products based on these oxides, but also to the degree of knowledge of its the colloidal-chemical properties. However, the variety of catalytic reactions and conditions requires the development of highly efficient catalytic systems based on other compounds for example binary oxides, carbides, and nitrides of various metals, in particular CeO_2-ZrO_2, MoO_3-WO_3 oxides and binary carbides Mo_2C-W_2C. These systems exhibit catalytic activity in many important reactions, including the conversion of light hydrocarbons. Necessity to develop import-substituting technologies in this area gives a special relevance to this thesis.

For the targeted implementation of the sol-gel method for different types of catalyst preparation, it is necessary to develop colloidal-chemical bases of this method, including to development of method for the synthesis of aggregative stable concentrated binary oxides hydrosols, to determination of their main colloidal-chemical properties, to develop the main stages of catalytic systems preparation and to reveal the fundamental relationship between conditions of each stage of the process and the properties of the final product.

The synthesis of binary compounds hydrosols is not only of practical but also of significant theoretical interest. There are several compounds that can be synthesized in the form of aggregative stable sols. A special place among this series is occupied by hydrosols SiO_2, ZrO_2, TiO_2, AlOOH, as well as molybdenum oxides of variable oxidation states (molybdenum blue). These disperse systems has anomalously high aggregative stability. In terms of their properties (constancy of dispersion over time, stability to the addition of electrolytes), these sols are close to lyophilic dispersed systems.

The stability of the mentioned hydrosols is due to the presence of developed surface layers on the particles. Under certain conditions, charged and highly hydrated layers, called gel layers, are formed on the particle surface. This leads to a decrease in interfacial tension and the appearance of repulsive forces due to electrostatic and structural factors. In such systems, with a sufficiently small particle size, conditions can be created that meet the Rebinder-Shchukin lyophilicity criterion, that is, these systems become lyophilic. This feature - the formation of developed surface layers on the surface of particles, can be used in the synthesis of hydrosols of binary compounds, one of the components of which will be an oxide with a lyophilized surface, and the other component will not have such pronounced properties. Information on the factors providing the lyophilicity of binary oxides will expand the understanding of the nature of the aggregative stability of metal oxide hydrosols.

The purpose of the dissertation was to develop a colloidal-chemical basis for a sol-gel process of perspective catalytic systems preparation based on hydrosols of binary oxides $Ce_xZr_{1-x}O_2$, as well as molybdenum and molybdenum-tungsten blue.

To achieve this goal, it is necessary to solve a few tasks, the most important of which were:

- development of new methods for synthesis of concentrated aggregative stable hydrosols, the particles of which are represented by binary oxides $Ce_xZr_{1-x}O_2$, and molybdenum and molybdenum-tungsten blue;

- determination of electro-surface, rheological and other colloidal-chemical properties of synthesized hydrosols, as a basis for development sol-gel technology of catalytic systems, as well as factors of their aggregative stability.

- development of the main stages of the sol-gel process of perspective catalytic systems based on hydrosols $Ce_xZr_{1-x}O_2$, molybdenum and molybdenum-tungsten blue.

- determination of the catalytic activity of systems based on $Ce_xZr_{1-x}O_2$ and Mo_2C-W_2C in the reactions of CO oxidation and dry reforming of methane.

Scientific novelty. New methods of synthesis have been developed and concentrated aggregative stable hydrosols $Ce_xZr_{1-x}O_2$, molybdenum and molybdenum-tungsten blues with different mole ratios of oxides and a narrow particle size distribution have been synthesized. The regularities of the formation of particles are revealed, the possibility of regulating their main characteristics is shown.

For the first time, systematic studies of the main colloidal-chemical properties of hydrosols of binary oxides $Ce_xZr_{1-x}O_2$ of molybdenum and molybdenum-tungsten blue, such as: composition, morphology, density, electrophoretic mobility of particles, have been carried out. The interval of pH of the aggregative stability of hydrosols and the coagulation thresholds in the presence of various electrolytes, as well as their rheological properties, have been determined. The

influence of the composition of particles, the synthesis conditions for their production on the basic colloidal-chemical properties of hydrosols has been established.

For the first time, the factors of aggregate stability of the systems were determined. It was found that the main contribution to the aggregative stability of $Ce_xZr_{1-x}O_2$, molybdenum, and molybdenum-tungsten blue hydrosols is made by the structural factor due to the presence of developed hydration layers on the particle surface.

The main stages of the sol-gel process for perspective catalytic systems preparation have been worked out. The regularities of the thermal decomposition of $Ce_xZr_{1-x}O_2$ xerogels of various compositions were revealed, the conditions for the formation of $Ce_xZr_{1-x}O_2$ solid solutions of various modifications and the features of the formation of a porous structure were determined.

The conditions for the synthesis of Mo_2C and Mo_2C - W_2C by thermal decomposition of molybdenum and molybdenum-tungsten blue xerogels were determined. The effect of a carbon-containing precursor (an organic reducing agent) on the morphology, phase composition, and porous structure of the carbides Mo_2C and Mo_2C - W_2C has been established.

Colloidal-chemical regularities of the preparation of supported and membrane catalysts based on $Ce_xZr_{1-x}O_2$ and Mo_2C - W_2C were established. Their high catalytic activity has been shown by the example of the CO oxidation reaction and carbon dioxide conversion of methane.

Practical significance. As a result of the research, new methods have been developed for the synthesis of concentrated aggregative stable hydrosols $Ce_xZr_{1-x}O_2$, molybdenum and molybdenum-tungsten blue, suitable for the preparation of catalytic materials.

The obtained experimental data and their theoretical generalization formed the basis for the development of a colloidal-chemical basis for the preparation of catalytic systems based on $Ce_xZr_{1-x}O_2$ and Mo_2C - W_2C.

The main stages for the preparation of supported $Ce_xZr_{1-x}O_2/Al_2O_3$ catalysts with reproducible properties have been developed and tested in CO oxidation reactions. The multicomponent catalyst $CuO/Ce_xZr_{1-x}O_2/Al_2O_3$ obtained by the sol-gel method exhibits activity comparable to the activity of catalysts based on platinum group metals.

Using hydrosols of molybdenum blue, the main stages of obtaining new type of catalysts - membrane catalysts with different architectures have been developed, which have shown high activity and efficiency in the reaction of carbon dioxide conversion of methane.

Defense Provisions

- An approach to the targeted synthesis of aggregative stable hydrosols of binary oxides $Ce_xZr_{1-x}O_2$ and molybdenum-tungsten blue with a lyophilized surface.

- The results of a comprehensive analysis of the main colloidal-chemical properties of hydrosols of binary oxides $Ce_xZr_{1-x}O_2$, molybdenum and molybdenum-tungsten blue, as well as factors of their aggregative stability.

- Conditions for carrying out the main stages of the sol-gel process to obtain supported and membrane catalysts based on $Ce_xZr_{1-x}O_2$and Mo_2C-W_2C, methods for controlling the morphology of the catalytic layer.

- Results of catalytic tests of samples of supported and membrane catalysts synthesized using $Ce_xZr_{1-x}O_2$ hydrosols, molybdenum and molybdenum-tungsten blue, confirming the efficiency of the sol-gel method for the synthesis of the listed catalytic systems.