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# Colloidal-chemical fundamentals of the sol-gel method for the preparation of ceramic membranes with deposited layers of manganese and cobalt oxides

## Abstract

**Relevance of the research topic**

There is a great deal of scientific interest in catalysts deposited by aggregatively stable aqueous dispersions of $MnO_2$ sols on the surface of microporous ceramic membranes based on $\alpha$–$Al_2O_3$. The filtration method is most commonly used to create a thin coating of active components, it is cost effective, has so many advantages and can be used to achieve a given reproducible layer thickness. Modification of the carrier surface coated with manganese dioxide nanoparticles is carried out to give it qualitatively new properties that can act as a catalyst in oxidation reactions not only in the gas phase, but also in the liquid phase, in particular, in the treatment of wastewater from various pollutants, such as: azo dyes, methylene blue, and others.

During the development of technology, many researchers faced the fact that $MnO_2$ nanoparticles have insufficient adhesion to the surface of aluminum oxide, even after heat treatment of the final product. Nowadays, there are many membranes made of silicon oxide, titanium oxide, or membranes with additional coated layers of zirconium and titanium oxides. However, these products are significantly more expensive. Hence, it was decided to apply an intermediate layer on the surface of the membrane element. The research aims to provide sufficient adhesion between the layer of manganese dioxide and the surface of the membrane. Cobalt oxide was chosen as the material for obtaining such a sublayer since it has exceptionally high adhesion to the surface of aluminum oxide, high chemical resistance in a wide range of pH values, including strongly acidic and strongly alkaline regions.

One of the most effective catalysts for liquid-phase oxidation reactions is to be mixtures of manganese and cobalt oxides. Such hybrid composites exhibit a higher catalytic activity compared to single oxide nanoparticles in the degradation of some organic dyes. However, there is no mention of the synthesis of sols of such oxides or basic salts of manganese and cobalt. The development of methods for the synthesis of aggregatively stable sols of oxygen-containing compounds of mixtures of manganese and cobalt will open up wide possibilities for obtaining catalytically active layers on the surface of ceramic membranes. At the same time, for the reproducible synthesis of materials by the sol–gel method, it is necessary to have a complex of knowledge about the basic colloidal–chemical properties of sols (phase composition, particle size, aggregation stability, etc.).

Conducting such studies is interesting from scientific and practical points of view and can be considered very relevant in terms of the possible use of such coated ceramic membranes in important areas.

**Purpose of the work:** development of colloid-chemical basics of the sol gel method for the preparation of ceramic membranes with deposited catalytically active layers using cobalt oxide and manganese dioxide sols.

Within the framework of achieving the goal of the dissertation work, it is necessary to solve the following **tasks**:

1. To master the methods for the synthesis of aqueous dispersions of nanoparticles of cobalt and manganese oxide, to determine their main colloidal chemical properties;

2. To develop a method for obtaining deposited layers of cobalt and manganese oxides, and to stabilize manganese dioxide nanoparticles in the deposited layer on the outer surface of tubular ceramic membranes by introducing nanoparticles of cobalt oxide as a sublayer;

3. To obtain the samples of deposited layers using sols of manganese dioxide, and mixed sols containing nanoparticles of both manganese dioxide and cobalt oxide, synthesized in the presence of various reducing agents and determine the main characteristics of the samples obtained;

4. To evaluate the catalytic activity of the resulted membranes with deposited layers in the reactions of decomposition of hydrogen peroxide and methylene blue dye in dilute aqueous solutions.

**Scientific novelty of the work**

1. Methods for the synthesis of aqueous dispersions nanoparticles of mixture of manganese and cobalt oxides sols synthesized in the presence of various reducing agents have been developed and the main colloid-chemical properties of $Co_3O_4$-$MnO_2$ sols have been studied.

2. A technique for obtaining deposited layers on the surface of tubular ceramic membranes using sols, similar to the filtering method, has been developed. A set of data was obtained on the properties of layers deposited on the surface of a ceramic membrane and on the surface of a $Co_3O_4$ sublayer, depending on using $MnO_2$ sol and deposition conditions.

3. A set of data was obtained on the catalytic activity of the obtained tubular ceramic membranes with deposited layers in the decomposition of hydrogen peroxide and in the decomposition of organic dyes methylene blue (adsorption-degradation-desorption process) in the presence of hydrogen peroxide in dilute aqueous solutions. The influence of annealing temperature (400, 500 and 600℃) on the characteristics of tubular membranes with a deposited layer of $Co_3O_4$ and $Co_3O_4$-$MnO_2$ was analyzed, including testing in the catalytic decomposition of $H_2O_2$.

**Theoretical and practical significance of the work**

The colloid-chemical foundations of the sol-gel method have been developed, which makes it possible to obtain catalytically active membranes with deposited layers based on $MnO_2$ and a mixture of $Co_3O_4$-$MnO_2$. A set of data has been obtained that makes it possible to establish the relationship between the conditions for the preparation of sols and the characteristics of deposited catalytically active layers.

The relationships obtained can be further used in scaling up the deposition process to obtain semi-industrial and industrial samples of catalytically active membranes. The developed catalytically active membranes can be used in wastewater treatment, combining the stage of filtration from coarse impurities with catalytic decomposition of water-soluble organic compounds, in particular, from azo dyes, methyl orange, methylene blue.

**The main provisions for the defense:**

- influence of the conditions for the synthesis of sols of manganese and cobalt oxides on the properties of the resulting membranes with deposited layers.

- influence of application conditions and calcining temperature on the properties of the resulting membranes with deposited $Co_3O_4$ and $MnO_2$ layers.

- the influence of the conditions for the synthesis of sols and the conditions for obtaining membranes on the catalytic activity of the obtained deposited layers.