Receiving thin films of active component on surface of glass-fiber catalysts by method of reactive magnetron sputtering

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Abstract. The technology for high-performance glass-fiber catalysts (GFC) on the basis of reactive magnetron sputtering to produce a thin film based on transition metal oxides with high adhesion to the support and film homogeneity in composition has been developed. Catalysts are appointed for environmentally friendly disposal of liquid hydrocarbon wastes and sludge with a reduction in gas emissions with possible further processing.

1. Introduction

Recycling and environmental disposal of liquid hydrocarbon waste and sludge is an important task in the field of environmental protection. Due to the high growth rate of production of modern oil producing and oil refining companies for decades, a significant amount of waste and sludge has accumulated on the territory of factories and in production sites. Annually there is an increase in waste up to 0.1% of the volume of processed oil in accordance with technological standards leading to an exasperation of the environmental situation which represents a significant danger to the society and the economy of the state.

Processing and disposal of liquid hydrocarbon waste and sludge is made with support of using various technological methods depending on their composition. At the same time, an important requirement for such technologies is their high environmental, energy and economic efficiency. This set of requirements is most consistent with the technology based on catalytic combustion. Traditionally enterprises use granulated catalysts in this area in which as an active component (Pt, Pd) or oxides of transition metals are used which are characterized by a low burning temperature with high thermal stability. However such catalytic systems are characterized by substantial diffusion inhibition of catalytic reactions as well as (in the case of granular catalysts) high hydraulic resistance.

Significant progress in this area has been made recently through the use of catalysts based on glass-fiber supports. The main advantage of GFCs is the possibility of forming structured catalytic cartridges with a uniquely high ratio of mass transfer intensity to specific hydraulic resistance. Such catalysts are original, have no foreign analogues, and have a high potential both in the field of import substitution in strategic areas and in the development of high-tech exports.

At the same time, the existing GFCs are characterized by an uneven distribution of the active component over the surface of glass-fibers, which negatively affects the observed activity of such catalysts. Glass-fiber materials as a rule have low values of textural characteristics (specific area – $S \sim 0.4$ m²/g, pore volume – $V \sim 0.001$ cm³/g, pore diameter – $d \sim 10.1$ nm), which contributes to poor fixation of
active component (example vanadium pentoxide) on the surface in consequence of which it exhibits low specific activity.

2. Materials and methods
At the work [1] the method of surface thermosynthesis of vanadium oxide catalysts based on structured microfiber supports is presented. The glass-fiber material was pre-impregnated with solutions of the compounds of the precursors of the active component. The support moved through the high-temperature zone the thermal effect of which initiated the course of the redox reaction (the oxidizer is oxygen of the air) as a result of which the phase of the active component was formed. The obtained samples of catalysts had a relatively low adhesion of the oxide film to the support and an uneven distribution of the active component over the surface of the glass-fibers.

The method of vacuum reactive magnetron sputtering [2, 3] makes it possible to obtain thin films of the active component with high adhesion to the glass-fiber support uniform distribution of the active component over the surface of the support and uniform distribution of the concentration of oxide elements throughout the film thickness. Spraying the particles of the active component in the vacuum chamber eliminates the appearance of contaminants on the surface of the support. The method makes it possible to relatively simply vary the composition of the film and rather accurately control the thickness of the film being grown which eliminates material overruns.

These experimental works are performed on the existing types [4, 5] and newly synthesized glass-fiber catalysts based on transition metal oxides developed for oxidation of volatile organic compounds.

Spraying the active component of the film was performed in a magnetron module NT-MDT complex NANOFAB 100. The stoichiometry of the resulting film depends on the ratio of the partial pressures of Ar and O$_2$ gases and, accordingly, on the ratio of the volume flow rates of gases entering the reactor chamber. At ratios of Ar/O$_2$ consumption below 5/1, the metal in the sprayed oxide is guaranteed to take the highest oxidation state and the oxide gets the corresponding oxidation state stoichiometry – V$_2$O$_5$. Electromagnetic valves on the gas lines of the installation allow you to adjust the flow rate of gases with an accuracy of 0.1 cm/min. The diameter of the sprayed target is 78 mm. Vacuum preparation of the reactor chamber was performed at a pressure of 5∙10$^{-5}$ Pa. The deposition was performed in a pulsed magnetron mode at a constant power of 125 W and a constant pressure of 0.25 Pa. Argon consumption to maintain the working pressure was 22 cm$^3$/min, oxygen consumption was 8 cm$^3$/min.

3. Results
The method of reactive magnetron sputtering allowed to put particles on the surface of glass-fiber material without secondary support in the vacuum chamber eliminating the appearance of impurities and to obtain thin films ~ 30 nm thick with high adhesion and uniformity in composition (figure 1).

![Figure 1](image-url). The surface topology in the secondary electrons of the JSM-6510LV-EDS electron microscope of the GFCs samples (V$_2$O$_5$/GFC) obtained by the method: (a) – surface thermosynthesis; (b) – reactive magnetron sputtering.
The inter fiber space is filled with particles of the active component (V$_2$O$_5$) with sizes from 5 to 15 nm which is associated with the deposition technology. The surface of the glass-fiber material in all experimental samples is covered uniformly. The applied active component is resistant to external mechanical stress when compared with other methods of synthesis.

4. Conclusion

Thus, the problem of increasing the specific activity of GFCs has been solved by applying the active component on the original glass-fiber support by the method of reactive magnetron sputtering. The method allows spraying the particles of the active component in a vacuum chamber, excluding the appearance of contaminants on the support surface and producing thin films with high adhesion to the substrate and high uniformity of the film in composition. An important advantage of this method is its wastelessness and the possibility of using inexpensive and affordable silicate glass fabrics as a carrier.

Acknowledgment

The work was performed in the framework of the project of the Russian Science Foundation No. 18-73-00285 of the Presidential Program for Research Projects.

References

[1] Mikenin P, Tsyrulnikov P, Kotolevich Y and Zagoruiko A 2015 Catalysis in industry 1 64–9
[2] Udovichenko S Yu, Bobylev A N, Belotserkovtseva D A and Shpindyuk D D 2018 Journal of Physics: Conference Series: Materials Science and Engineering 387 012080
[3] Bobylev A N and Udovichenko SYu 2016 Russian Microelectronics 6 396–401
[4] Zazhigalov S and Elyshev A 2017 Reaction Kinetics, Mechanisms and Catalysis 1 247–60
[5] Mikenin P, Zazhigalov S and Elyshev A 2016 Catalysis Communications 87 36–40