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COLLOID-CHEMICAL FOUNDATIONS OF SOL-GEL SYNTHESIS OF MEMBRANE CATALYSTS WITH VARIOUS ARCHITECTURES BASED ON Mo_2C

Speciality 1.4.10 – Colloid chemistry

Dissertation Abstract for the Degree of Candidate of Chemical Sciences

An analysis of the current market for russian industrial catalysts reveals a significant decline in the areas of their development, product range updates, and production modernization. As a result, the share of imported catalysts for oil and gas processing accounts for 60 % (supplied by Grace, UOP, Axens, BASF, etc.). This situation does not align with the national interests and economic security of Russia. Therefore, the development of new efficient catalysts, including in the field of light hydrocarbon processing, is a highly relevant task.

High-temperature reactions of light hydrocarbon transformations are accompanied by considerable diffusion limitation, as a result of which the surface of the catalyst — usually expensive — is used by no more than 7 %. Therefore, there is great interest in conducting chemical transformations in membrane catalytic reactors (MCR) using membrane catalysts. Here, membrane catalyst represents a composite membrane with a bimodal porous structure, consisting of an inert support featuring large transport pores and a catalytically active substance distributed across it, with a developed meso/microporous structure. Due to differences in the porous structure of the support and the catalyst, various mass transfer mechanisms may arise. In such cases, the catalytic process can be intensified both through the effective composition of the catalyst and through influencing mass transfer within its porous structure.

For example, the reaction rate of dry reforming of methane (DRM), which is considered a promising method for producing synthesis gas with a specific H_2/CO ratio,

increases more than 30-fold in MCR compared to a conventional fixed-bed reactor when using membrane catalysts with a specific porous structure. The reason for this phenomenon is related to the intensification of mass transfer in the porous structure of membrane catalyst due to the occurrence of thermal creep. It is known that thermal creep can only be observed under certain conditions (pressure, temperature, composition of the reaction mixture) and within pores of a specific size range. Thus, the synthesis of membrane catalysts with various structures and architectures is an important task for the further development and implementation of membrane catalysts in conducting various high-temperature reactions.

The sol-gel method is a flexible, scalable approach for producing coatings, films, selective layers, and catalysts, one variant of which is based on the use of stable nanoparticle dispersions. Molybdenum carbide is considered a promising alternative to expensive platinum group metals. Among its advantages are catalytic activity similar to that of noble metals, resistance to sintering, coking, and the effects of many catalytic poisons. Molybdenum blues is as a promising sol-precursor for Mo_2C-catalyst, where particles are represented by highly dispersed, nearly monodisperse polyoxomolybdate clusters with sizes no larger than 5 nm. Al_2O_3 oxides and $Ce_{0,5}Zr_{0,5}O_2$ solid solutions are successfully used as mesoporous support materials. Therefore, developing the synthesis of MCs with various architectures based on Mo_2C using the sol-gel method is highly promising.

The aim of the work is to develop the colloid-chemical foundations of sol-gel synthesis of membrane catalysts with various architectures based on Mo_2C.

Reserch tasks:

1. Determine certain colloid-chemical properties of AlOOH and molybdenum blue sols, the knowledge of which is necessary for developing the foundations for producing MC with a specified architecture (particle size, shape, ζ-potential; dependence of these characteristics on the pH of the dispersion medium; rheological properties).

2. Develop a method for producing a defect-free sublayer of a mesoporous support with the required phase composition on the outer surface of a porous substrate using boehmite and $Ce_{0,5}Zr_{0,5}O_2$ sols that do not contain additional additives.

3. Synthesize membrane catalyst with a top Mo_2C layer on the outer surface of a porous substrate (Mo_2C/α-Al_2O_3), membrane catalyst with uniform distribution of Mo_2C across the initial substrate (Mo_2C/α-Al_2O_3), and membrane catalyst with Mo_2C distributed across a mesoporous support layer of γ-Al_2O_3 (Mo_2C/γ-Al_2O_3/α-Al_2O_3).

4. Synthesize membrane catalyst with mesoporous $Ce_{0,5}Zr_{0,5}O_2$ uniformly distributed across the initial substrate ($Mo_2C/Ce_{0,5}Zr_{0,5}O_2/\alpha$-$Al_2O_3$) and across a γ-Al_2O_3 sublayer ($Mo_2C/Ce_{0,5}Zr_{0,5}O_2/\gamma$-$Al_2O_3/\alpha$-$Al_2O_3$).

5. Establish the influence of heat treatment conditions for molybdenum blue xerogels on the phase composition, morphology, and porous characteristics of the resulting molybdenum carbides.

6. Determine the catalytic activity of membrane catalysts with different architectures in the DRM reaction and establish the relationship between the porous structure characteristics of MC and their catalytic activity.

The following are submitted for defense:

1. Data on the colloid-chemical and rheological properties of boehmite and molybdenum blue sols;

2. Conditions for producing a mesoporous sublayer on a porous α-Al_2O_3 substrate based on boehmite sols with thicknesses from 1.0 to 3.0 μm and a predominant pore size of 22 nm;

3. Conditions for producing molybdenum carbide from molybdenum blue xerogels using three different methods;

4. Results of kinetic experiments in the DRM reaction on membrane catalysts of various compositions and architectures in a membrane reactor operating in contactor mode with diffusion mass transfer.

Scientific novelty

1. For the first time a comparison between the conditions of thermal decomposition of molybdenum blue xerogels in various media and the porous characteristics and phase composition of the resulting molybdenum carbides has been made.
2. For the first time a method for producing a massive Mo_2C catalyst layer on a porous α-Al_2O_3 substrate using chemical modification of the initial substrate with a PEG solution has been developed.
3. For the first time the influence of the $[H^+]$:[Al] ratio during boehmite sol synthesis on the characteristics of the γ-Al_2O_3 layer (thickness and morphology) obtained by depositing this sol has been established.
4. For the first time kinetic studies of the DRM reaction have been conducted using MC of compositions Mo_2C/γ-Al_2O_3/α-Al_2O_3 and $Mo_2C/Ce_{0,5}Zr_{0,5}O_2$/γ-$Al_2O_3$/α-$Al_2O_3$, and rate constants have been determined for membrane catalysts with different structures.

Practical significance

A method has been proposed for calculating the thickness of layers produced by depositing boehmite sols with different concentration-viscosity characteristics, taking into account capillary filtration and film coating occurring simultaneously during single dip-coating of porous cylindrical substrates. This method allows calculating the required deposition parameters (dip/withdrawal speed, holding time) for boehmite sol to obtain a layer of specified thickness.

Three scalable methods for producing molybdenum carbides have been developed, based on thermal decomposition of MB xerogels, which allow producing carbides with different phase compositions (β-Mo_2C, α-Mo_2C, α-Mo_2C/η-Mo_2C/C) and different porous structure characteristics (specific surface area $S_{уд}$ — from 1,5 to 175,0 m^2/g, and mesopore volume up to 0,03 sm^3/g). Samples of MC based on Mo_2C have been obtained, which increase the specific catalytic activity of the catalyst by 115-fold compared to powdered Mo_2C.

Thesis to be defended:

1. Data on the colloid-chemical and rheological properties of boehmite and molybdenum blue sols have been obtained, enabling the synthesis of membrane catalysts with various architectures.

2. A method for producing a defect-free γ-Al_2O_3 sublayer with a developed mesoporous structure on the outer surface of a porous α-Al_2O_3 substrate by dip-coating in boehmite sols without introducing plasticizers or viscosity regulators has been developed. It has been established that the morphology and thickness of the layer are influenced by the $[H^+]$:[Al] ratio during peptization in the course of boehmite sol synthesis.

3. A method for calculating the thickness of γ-Al_2O_3 layers produced by depositing boehmite sols has been proposed, which allows transitioning to the production of mesoporous boehmite-based coatings with a specified thickness. It has been determined that both the «capillary filtration» regime and the «film coating» regime must be taken into account for the calculation.

4. An MC with a Mo_2C layer on the outer surface of a porous substrate has been synthesized, with no particle infiltration into the substrate interior. Optimal conditions for depositing 2 wt.% molybdenum blue sols on PEG-modified substrates have been established (dip/withdrawal speed: 60 mm/min, no holding time) to obtain a uniform layer approximately 2 μm thick.

5. A set of data on the formation of molybdenum carbides from MB xerogels using various heat treatment methods has been obtained. It has been found that molybdenum carbides with the highest specific surface area (175 m^2/g) are formed as a result of thermal decomposition of MB in an inert atmosphere upon heating to 900ºC. The possibility of varying the phase composition of the carbides has been demonstrated. When the $[C_6H_{12}O_6]$:[Mo] ratio is < 7, α-Mo_2C/C is formed; with an increase in this ratio, carbides of the composition α-Mo_2C, η-Mo_2C, and C are formed. β-Mo_2C is produced as a result of temperature programmed carburization (TPC) of MoO_3 obtained by calcining MB xerogels.

6. Based on kinetic experiments on conducting the carbon dry reforming of methane process in a membrane reactor in contactor mode using MCs of various architectures, an increase in their catalytic activity has been established with increasing pore volume, corresponding in size to the occurrence of activated mass transfer (due to thermal slip). It has been shown that selecting the MC architecture allows increasing catalytic activity by more than twofold. The use of an additional $Ce_{0,5}Zr_{0,5}O_2$ layer enhances the resistance of Mo_2C-based MCs to deactivation. Compared to a powdered Mo_2C catalyst produced by heat treatment of MB xerogels in an inert atmosphere, the catalytic activity of MCs based on it is 115 times higher.