Scientific and technological foundations for the formation of membrane catalysts for methane conversion processes

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Relevance of the research topic

One of the important tasks in creating compact units for processing hydrocarbon raw materials is to reduce the size of the reactors, as well as to reduce the number of technological stages in the process while maintaining the required productivity. This can only be achieved on the basis of a reliable kinetic model that takes into account the mechanism of the process and the kinetics of the reactions occurring in the pore space of the membrane catalyst (MC). Without an understanding of these patterns, it is impossible to move to an optimal reactor design and the correct scaling of the process.

The development of compact, efficient, and energy-independent natural gas conversion units is unthinkable without the use of new physical foundations and technological principles, as well as new materials (in particular, catalysts) and engineering solutions. One of the development areas is membrane catalysis, which will make it possible to effectively control mass transfer in high-temperature catalytic processes and ensure the coupling of exo- and endothermic reactions. The creation of reactors with membrane catalysts is impossible without kinetic studies that provide an understanding of the mechanisms of such processes and their proper use.

Dry reforming of methane (DRM) is an endothermic process in which two greenhouse gases are used as reagents. It proceeds at high temperatures and requires high energy input. Most of the components of the reaction mixture in DRM are simple gases that are easily detected by modern chromatographs, which significantly facilitates labor-intensive kinetic studies. Despite the fact that DRM is characterized by a significant endothermic effect, the combination of this process with exothermic stages involving oxygen can form the basis for creating small-scale and

environmentally attractive plants for the production of syngas and its products. Given that the productivity of reactors with a porous membrane catalyst (PMC) is orders of magnitude higher than that of dense MCs, their application appears promising for carrying out the conversion of natural gas under autothermal conditions.

Objective of the work

Experimental identification of the patterns of oxidative dry reforming of methane (ODRM) by coupling dry reforming of methane and oxidation of methane with molecular oxygen in a reactor with a porous membrane catalyst.

Research tasks:

1. Kinetic analysis of dry reforming of methane in the contactor, extractor, and distributor modes in a reactor with a porous membrane catalyst, and selection of the reactor mode for the combined oxidative dry reforming of methane process.

2. Production of a porous membrane catalyst that is stable under conditions of oxidative dry reforming of methane, based on molybdenum and tungsten compounds, using the method of chemical deposition from vapor-gas mixtures of molybdenum and tungsten carbonyls.

3. Research into porous membrane catalysts in the processes of DRM and oxidative dry reforming of methane.

4. Analysis of the obtained results and justification of the kinetic scheme for the oxidative dry reforming of methane.

Scientific novelty

The scientific novelty of the study lies in the coupling of the processes of methane oxidation by carbon dioxide and molecular oxygen on a PMK and the interpretation of the obtained results within the framework of the hypothesis about mass transfer by thermal sliding in the pore channels of the membrane catalyst. For the first time, the experiment in a reactor with a PMK was supplemented by the direct determination of heat costs in the processes of natural gas conversion, which made it possible to obtain objective energy estimates of heat losses to the

environment, heat losses in the dry reforming of methane, and compensation for heat losses in the combined process of ODRM.

For the first time, the phenomenon of temperature inversion has been observed in a reactor with a membrane catalyst during the transition from the DRM process to the combined ODRM process. The interpretation of this phenomenon as a consequence of mass transfer and mass exchange in the catalytic process on the PMK can be considered as an extension of the hypothesis about active mass transfer by thermal slip in a heterogeneous reaction in the narrow pore channels of the catalyst.

A kinetic scheme has been proposed, based on the oxidation of carbon deposits during the oxidative dry reforming of methane. Instead of the reaction of carbon deposits being oxidized on the catalyst surface by carbon dioxide, the reaction of complete oxidation of carbon by oxygen has been included.

Theoretical and practical significance

The theoretical significance lies in the development of the hypothesis about mass transfer in pore channels of submicron dimensions due to thermal slip and in applying a kinetic experiment to a catalytic process in a membrane reactor, in which the PMC ensures active mass transfer in the pore channels and, thus, ensures the coupling of endo- and exothermic processes. It has been shown that the hypothesis of active mass transfer provides a good explanation for the features of the coupling of such processes and the temperature inversion. Such coupling can be considered as a "mechanism" that ensures the transition from one thermodynamic state to another. Managing such a transition could serve as the basis for developing autothermal methane conversion processes and, in the future, for other hydrocarbons.

The practical significance lies in the fact that establishing the process mechanism and its kinetic modeling make it possible to proceed with scaling up the process and designing a reactor with a membrane catalyst.

The main provisions for the defense:

1. Methane conversion on a porous membrane catalyst is a complex heterogeneous-homogeneous process of converting methane into syngas, in which heterogeneous stages (methane cracking, gasification of carbon deposits with water vapor, carbon dioxide, and oxygen) occur on the walls of the pore channels, and the composition of the syngas is formed from the products of these stages in the homogeneous reverse water-gas shift reaction. At the same time, mass transfer in the pore channels is determined by the phenomenon of thermal slip, which occurs in the near-wall gas layer of the pore channel in the catalytic layer of the membrane catalyst.

2. A method has been developed for preparing porous membrane catalysts by co-depositing molybdenum and tungsten carbonyls onto a porous ceramic substrate from a vapor-gas mixture of argon and the metal carbonyls, followed by activation of the resulting metal oxides in a temperature-programmed reduction process in a mixture of argon and hydrogen.

3. A methodology has been proposed for studying coupled catalytic gas-chemical processes for the production of syngas in a reactor with a porous membrane catalyst by transitioning from dry reforming of methane to oxidative dry reforming of methane.

4. Interpretation of the phenomena (temperature inversion, compensation for losses to the environment in the oxidation reaction of carbon deposits) observed during the oxidative dry reforming of methane, based on the hypothesis of mass transfer by thermal sliding and mass exchange through the pore channels of the membrane catalyst between adjacent parts of the reaction space.

5. Justification of the kinetic scheme for the intermediate stages of oxidative dry reforming of methane.