Intensification of dry reforming of methane in a reactor with a membrane catalyst

Gubin Sergei Aleksandrovich

Relevance of the study. In his book «Physical Methods of Intensification Chemical Engineering Processes» G.A. Kardashev cites the following quote: «The traditional basis for developing chemical engineering processes and apparatuses was formed many decades ago and, as a rule, does not contain new achievements in physics and achievements in related areas of technology». This statement can be fully applied to both catalytic and membrane-catalytic processes.

Existing industrial processes have indeed exhausted their potential for improvement, both as a result of improving the chemical composition of catalysts and improving the reactors for their use. After Academician V.M. Gryaznov discovered membrane hydrogen extraction on selective palladium films, it seemed that it was possible to change the thermodynamic equilibrium in catalytic processes and thus intensify them. However, the low permeability of membranes based on palladium and its alloys made their use economically inexpedient. Attempts to achieve a similar effect on porous membranes were also unsuccessful due to the low selective permeability of membranes and membrane catalysts.

Along with the above, it should be noted that for several decades, the facts observed by a number of researchers indicating the possibility of intensification of gas-phase reactions on membrane catalysts (MC) remained unexplained. There are scattered attempts to compare a conventional catalytic reactor and a membrane reactor, but not in all such publications did the authors observe the intensification effect. Perhaps this is due to the choice of a certain type of membrane reactor (MR), which was chosen for comparison.

In MR the catalyst can be located on the membrane itself (or the membrane can act as a catalyst) or be located as an independent layer, localized in different parts of the reactor from the membrane (for example, being located as a fixed-bed catalyst (powdered catalyst (PC)) inside or outside the selective membrane). In each of these reactors, several modes (concepts) can be implemented, which will

differ in the method of feeding reagents into the reactor and removing the reaction mixture from them.

The contactor mode can be implemented only in a reactor with a membrane catalyst, such a reactor is called a membrane catalytic reactor (MCR). A type of contactor is a forced flow-through contactor, in which the reactants are forcibly transported through the MC. This mode is especially promising for fast reactions, in which kinetic limitations caused by intra-diffusion inhibition often manifest themselves. It was in this MC mode that the intensification of the dry reforming of methane was discovered.

Purpose of the study. Determination of the mechanisms of mass transfer of substances and the degree of intensification of dry reforming of methane by comparing the kinetic parameters of this reaction in reactors with powder and membrane catalysts.

To achieve this goal it was necessary to solve the following **tasks**:

1. Conduct a kinetic experiment and compare the indicators of DRM in MCR with MC and in a conventional reactor with PC;
2. Study the DRM on the MC in the «diffusion» transport mode and compare the results with the «forced» transport mode;
3. Calculate the Knudsen numbers for all gases under the conditions of DRM and determinate the gas flow regime in the pores of the MC;
4. Calculate and compare methane flux densities under isothermal conditions (experiment to determine the effective diffusion coefficient) and under non-isothermal conditions (kinetic experiment);
5. Determine the rate constants of all intermediate stages of the DRM process on membrane and powder catalysts;
6. Based on the analysis of kinetic data, research of the characteristics of the pore structure and mass transfer characteristics of the MC, make a conclusion about the features of mass transfer in the pore structure of the MC under DRM conditions.

Scientific novelty:

1. For the first time it was established that the reason for the intensification of DRM on the MC is activated mass transfer in the pore structure, based on the phenomenon of thermal creep;

2. Based on the concept of thermal creep, a kinetic scheme of the DRM process is proposed, which, being the main scheme for the PC process, is supplemented with an equation for the gasification of carbon deposits with water vapor formed in the reverse shift reaction of «water gas»;

3. It has been confirmed that the specific rate constant of methane cracking in a reactor with MC is 30 times greater than the same constant in a conventional reactor with PC;

4. Effective diffusion coefficients for methane and carbon dioxide on MC under isothermal conditions were experimentally established. It was shown that the effective diffusion coefficients for methane, determined in mixtures with different inert gases, are close to each other. In addition, the effective diffusion coefficients for CH_4 and CO_2 are related to each other as the square root of the ratio of the inverse molecular masses of these reagents. All this indicates the occurrence of Knudsen diffusion in the pore structure of MC;

5. A complete kinetic analysis of dry reforming of methane was carried out and it was shown that heterogeneous reactions at intermediate stages of the DRM proceed under conditions of rarefied thermal slip flow, as irreversible, and the chemical equilibrium in them is «shifted» towards the formation of products. In this case, reactions involving substances with a lower molecular weight have the highest probability, and homogeneous reactions of reagents and products of the DRM reaction are impossible under these conditions due to the deficiency of intermolecular collisions. In the reactions of gasification of carbon deposits formed in the cracking reaction, competition arises between the reactants - carbon dioxide and water vapor.

Theoretical and practical significance of the study. It has been shown that for the intensification of heterogeneous gas-phase reactions and for reversible reactions occurring with an increase in the volume of products, for shifting the chemical equilibrium up to complete irreversibility, it is advisable to obtain a porous structure of membrane catalysts ensuring the occurrence of mass and heat transfer in them based on thermal creep.

The use of membrane catalysts with a porous structure ensuring the emergence and existence of heat and mass transfer based on thermal creep will make it possible to create high-performance and small-sized reactors for various heterogeneous and gas reactions.

The obtained results allow us to begin scaling and designing apparatus for producing syngas and hydrogen from natural gas.

Methodology and research methods. The research methodology consists of the combined use of methods for obtaining and studying conventional catalysts and membranes. The kinetic method was used to study the catalytic properties of membrane catalysts, and the methods used in membrane technology were used to study the transport characteristics.

Provisions submitted for defense:

1. Realization of the DRM in the MCR leads to the intensification of the process;
2. Excess pressure at the inlet to the MCR operating in contactor mode does not affect the DRM performance;
3. Transport of substances in the pore structure of the MC is subject to Knudsen diffusion;
4. The phenomenon of thermal creep occurs on the surface of the MC pores;
5. Thermal creep and counter axial flow create a circulation loop;
6. Heterogeneous reactions occur in a rarefied state, and homogeneous reactions occur in a continuous state;

7. On a powder catalyst, water vapor is the final product of the DRM reaction, and on a MC, it is an intermediate reagent.