METAL-CARBON NANOSTRUCTURED MEMBRANE CATALYSTS

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Introduction

The membrane catalysts possess a selective permeability for one of the reagents. They are offered the decades ago and are applied for the intensification of some processes of chemical, petrochemical, medical and the food-processing industry and essential increase of selectivity of catalysts [1].

The carbon materials got the increasing value in processes of membrane catalysis and gas separation due to their high selectivity and permeability, high hydrophobicity and stability in corrosive and high-temperature operations. Recently many papers were published considering last achievements in the field of carbon membranes for gas separation [2-5]. In particular, many types of carbon membranes were obtained as a thin film on a porous material by the carbonization of polymeric predecessors. Publications about carbon membrane catalysts are not found up to now.

At the same time carbon materials are widely known supports of metal catalysts. It has been shown earlier, that the carbon supports increase the dehydrogenative properties of the metal catalysts due to the epitaxial changing of metal crystall structure providing their structural relevance with reacting molecules. [6].

The present work is the first sample to develop the methods of preparation of carbon membrane catalysts with metal nanoparticles in a carbon membrane matrix. The activity of obtained composite membrane catalysts is investigated in the model reactions of hydrocarbons dehydrogenation.

Results and discussion

The noncoherent IR radiation has been applied for the first time for a formation of the metal - carbon film on a surface of the porous inorganic support. The film was obtained from a mixture of polyacrylonitrile (PAN) and ammonium perrhenate solutions in dimethylformamide.

The film was annealed by intensive IR-radiation and was quenched up to a room temperature with a rate 10-20 K/s. The intensity of IR-radiation was controlled by the resulting temperature of a film (950-1050 K). The halogenic lamps KG - 220 (λ = 0,9 - 1,7 microns) were used as an IR-radiation source. The optimum size of molecular mass of polymer (100000 – 200000) allowed to obtain the stable defectless film on the porous substrate.

IR-radiation influences selectively on oscillatory energy of separate groups of a PAN macromolecule, allowing to operate in the certain limits of the chemical transformations, leading to formation of a carbon material. The reduction of rhenium salt in a PAN matrix and the formation of the polyconjugated polymer system proceed simultaneously and interdependently during IR-pyrolysis of a film. As result the thin film of carbon with ultradisperse metal particles is formed. The size of metallic particles was proved to be from 3 to10 nm

Granulated rhenium catalyst on the carbon support has been obtained in another way. Pyrolysis of a copolymer of acrylonitrile and divinylbenzene was carried out at the temperatures of 1150-1250 K. The obtained carbonisate was soaked preliminary by ammonium perrhenate (the maximal rhenium loading was 7 mas. per cent in recalculation on metal), was subjected to the further heat treatment in an inert atmosphere at 1450 K. The heating was carried out step by step. The gradual heating up to 950 K caused a decomposition of ammonium perrhenate to surface oxides in a porous carbon matrix. Then, the interaction of metal oxide with a carbon matrix, including the chemical and crystallochemical reactions, occurring frequently in parallel, give a Re-organic compound. The loss of nitrogen up to the maintenance of 1-2 % are observed at the temperatures as high as 1250 K. Simultaneously carbon reduces rhenium oxide to the metal rhenium and oxygen evolved interacts with a carbon surface, causing a porosity .

Crystal structure of this catalyst proved to be similar to a-silica structure (a = 4,90 Å, c = 5,4 Å), considerably distinguished from parameters of the lattice of graphite (a = 2,46 Å, c = 5,7 Å), and from that of rhenium carbide lattice (a = 2,74 - 2,81 Å). Carbide presence at the catalyst is not observed, as its decomposition on free metal and carbon takes place in annealing process. The "secondary carbon" formed has crystal graphite-like structure, and rhenium presents in intralayer space of graphite fragments, deforming considerably its hexagonal lattice.

X-ray diffraction pattern of the catalyst has no responses of crystal rhenium in the area of $2\Theta=2{,}0 \div 42{,}9$ grad. It does mean that atoms of rhenium present between the layers of graphite structure. At the same time XPS spectra contain two maxima at the bonding energy of 1,48 and 1,84 эВ, characteristic for rhenium.

The membrane catalyst, obtained by IR-pyrolysis of PAN and ammonium perrhenate, has shown activity in cyclohexane dehydrogenation at the temperatures from 500 to 700 K. The maximal benzene productivity was 1.76 mol/m^2 h at 673 K with the catalyst containing 5 % Re. The usual Re/C catalysts require Re loading as much as 30 % for achievement the similar activity at such operation conditions [6].

The activity of granulated rhenium catalyst, obtained from copolymer carbonisate, has been investigated in reactions cyclohexane or ethylbenzene dehydrogenation in plug flow conditions at temperatures from 650 to 900 K, the reagents feed of 30 - 100 ml/min and initial hydrocarbons partial pressure of 0,5 kPa. The catalysts stable work was observed for a long time without regenerations at high conversion of initial reagents.

Conclusions

1. The composite membranes containing on a surface a thin carbon film with a metal phase were obtained for the first time by using of the noncoherent IR-radiation. It is shown, that such catalysts demand considerably the smaller maintenance of metal, than the traditional catalysts put on coal, with other things being equal.
2. The granulated catalyst containing up to 7 mas. per cent of rhenium in a porous carbon matrix was obtained for the first time by high-temperature destruction of copolymers.

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