STATISTICAL WEIGHT OF FULLERENES FORMATION IN CATALYTIC INTERACTION CONDITIONS OF THE METHANE WITH THE WATER VAPOUR

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In work [1] formation nanostructure in conditions catalytic steam conversion (ККМ) of methane is considered: $CH_4 + H_2O = 3H_2 + CO$ (1) It is considered, that reaction (1) goes with absorption 206 kJ/mol and is total consisting of two endothermic stages: the first - reactions of decomposition of methane - $CH_4 = C + 2H_2$ (2) with thermal effect 75 kJ/mol and the second - gasification of carbon (taking place as nanostructure) - $C + H_2O = H_2 + CO$(3) with thermal effect 131 kJ/mol. Carbon is formed inside пор the catalyst as nanotube. Patterns for formation nanotube are micro dendrite nickel (МДН). This model of formation nanostructure proves to be true directly and indirectly independent experiments. Quantity of publications considerably[see journal"Carbon"USA]. It is represented probable, that besides nanotube in порах the catalyst can be formed fullerenes.

Interaction CH_4 with H_2O and formation CO and H_2 occurs inside pore the catalyst. A surface pore more than an external surface of granules of the catalyst more than in 10^5 times [2]. Therefore, for statistical model of definition of statistical weight of formation fullerenes (Gf) we shall allocate the idealized fragment of pore (ИФП). ИФП - cored the cylinder in diameter 30nm and 150nm.

The considered model is made for ККМ on experimental installation which design is described in [3] and industrial tests described in [4.] below described assumptions concern to conditions of works [3] and [4] where the layer of granules of the catalyst has the allocated zone of the most active reaction (ЗНАР) CH_4 with H_2O, however and in industrial furnaces it is possible to allocate quasi -ЗНАР.

As statistical weight of macro state (МАС) we shall understand number of ways of micro state (МИС) by which can be realized set МАС attributed to the general number МИС. Macro objects (МАО), statistical weight of formation which are required to be defined, are considered nanotube and fullerenes. МИС there will be discrete contacts (DK). DK - contact between micro objects (МИО), and also МИО with МАО. We shall designate МАО and МИО taking place inside ИФП. ИФП - open system. МАО is nanotube, МДН, molecules Al_2O_3 [1] making surface ИФП and fullerenes. Inside ИФП are 10 nanotube and 10 МДН. Their sizes are identical and represent the idealized continuous cylinders in diameter of 2nm and height 15nm. The basis of the cylinder is on internal surface ИФП, and the axis of the cylinder is directed to axis ИФП. Molecules Al_2O_3 are vibrators on internal surface ИФП. Al_2O_3 change with frequency 10^{12} - 10^{14} Hz. For one fluctuation energy up to 0,15 eV can be transferred. The area of a surface of the vibrator $20nm^2$. The last on transfer МАО in the present model isfullerene . We shall consider, that is formed only C_{60} though formation of other structures is possible. МИО the submitted model cooperating molecules are: CH_4 with H_2O and formed: C, H_2, CO. Each of the listed molecules has the characteristic geometrical form submitted in [5].

Here we shall specially note, that in offered model quantum character of interactions of objects is not taken into account. The problem is put to find out qualitative characteristics of interactions of molecular objects and their mutual transformation. As speeds of objects low (speeds of moving of objects in space are stacked in Maxwellian distribution (MD) for $T<1200K$) it is supposed, that molecules have the known geometrical form [5] which possesses properties of a macro body and, kinetic energy (Ек) both potential energy (Ep) and a impulse **(p)** not quantized.

МИС, i.e. DK we shall divide into three kinds of contacts: absolutely elastic impact (АУУ), elastic impact (УУ), absolutely not elastic impact (АНУ). Contacts АУУ - all this contacts МИО to vibrators and contacts: H_2O-H_2, H_2O-H_2O, H_2-H_2, H_2-C; CO, H_2O, H_2-МДН, H_2, CO - nanotube, H_2-CO, H_2-CH_4, CO-H_2O, CO - CH_4.

Fullerenes have АУУ contacts to all other objects. УУ contacts: CH_4-CH_4, CH_4-H_2O, H_2O-C, nanotube - H_2O, C. As a result of these recreation centers can, be formed whether or not others МИО. It depends on full energy of objects. Conditional, boundary size of full energy between АУУ and АНУ 0.6 - 1eV.

АНУ contacts it chemisorptions CH_4 on МДН and contact of atoms C. In the first case - are formed nanotube in the second an element Fullerene structures.

The vector of moving for all МИО is directed from one basis ИФП to another (input - output). The beginning of coordinate's ИФП on an axis of the cylinder on an input. In ИФП 20 pairs CH_4 and H_2O enter. The direction of a vector of speed (**v**) CH_4 and H_2O changes from 0 up to π. **|v|** submits to MD for 1100К. An interval of occurrence CH_4 and H_2O - 10^{-10}с. Poisson's distribution for CH_4 and H_2O on the area of basis ИФП and a direction of a vector of speed - is set. All micro objects, including and fullerene, have three degrees of freedom in space, rotate around of the center of weight and are not harmonious oscillator. Average time of a presence of separate micro object in ИФП - 5×10^{-7}с.

On an output from ИФП there are following objects: H_2, CO fullerene. Total probability of occurrence on output CH_4, CO_2 and H_2O - up to 0,1, but for simplification of a problem by their occurrence it is neglected.

Appearing inside ИФП МИО, collide with vibrators on a wall and receive Ек, first of all rotary Ек. Frequency oscillator МИО comes nearer in frequency of vibrators. Ек forward at increase of quantities of a recreation center turns in rotary Ек. It is connected by that the form of objects is not regular and is considerably extended (see [5]) and transfer **p** does not get in the center of weights. Moreover, position of the center of weights of object varies in time (oscillator nonharmonic) and transfer of energy from a body of smaller energy to a body with the greater energy by a rule of the lever is possible. МИО receive more and more rotary Ек and its transformation in Ep chemical connection begins at corresponding recreation centers. МДН not always can form , but can serve as a pattern for cycles C_5 and C_6 and fullerene. Rotary Ек can be more 2,5eV and CH_4 loses H then МИО - C can exist up to 10^{-6}с. On the submitted model it has turned out, that G nanotube = 0,007, and Gф = 0,07. Fullerene and МИО leave ИФП with **|v|** reduced up to PM corresponding T~250K, but with big rotary Ек. It proves to be true experimentally. At selection of gas tests from a layer of the catalyst (see a design in [3]). The metal tube had temperature 260К, and then at transformation rotary Ек in forward Ек was heated up up to 500К. The similar phenomenon was observed on an industrial pipe with ЗНАР [4]. The temperature of pipe ККМ was 1250К, the temperature of a by-pass pipe was 600К, and then the by-pass pipe was heated up to 1100К. A presence fullerenes proves to be true indirectly. At formation C_{60} it is allocated 4000Дж/моль. The thermal balance in ЗНАР [3] gives deficiency of brought heat. The account of formation C_{60} removes a question. The material balance gives overestimated stochiometric quantity H_2 above CO. At the account of formation C_{60} the balance is leveled.

Presence fullerenes can be checked up in technological gas of industrial tubular furnaces. Gas for the analysis on an output from a pipe is selected through filters. In filters should be fullerenes. At unloading the fulfilled catalyst of pipes ККМ on a site quasi-ЗНАР in pores the catalyst are fullerenes. The sizes of a site quasi-ЗНАР makes 1m. The note: Pressure (concentration of microobjects on a unit of volume) is significant at the exact decision of a task in view. Qualitative the analysis in an interval 0,5-20 Bar, allows to neglect pressure. Contact C_{60}-H_2O is conditionally qualified.

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