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A Gradientless Reactor for Kinetic Studies of Catalytical Processes at High Temperatures

Reaktor bezgradientowy do badań kinetyki procesów katalitycznych w wysokich temperaturach

Безградиентный реактор для исследований кинетики каталитических процессов в высоких температурах

The gradientless technique for determining the rate of catalytical reaction has more and more pushed out other traditional methods for a longer time. To determine the reaction rate rotating reactors, in which the catalyst [1-5] is placed, are most frequently used, as well as stirred gas reactors, where the catalyst is stationary [6-10].

DETAILS OF THE REACTOR

Many catalytic reactions take place at temperatures within 600-900°C. An example of such a process is steam reforming of methane. To carry out such a reaction both on pellets 20x20 mm, or on very fine catalyst particles, a reactor with internal circulation has been constructed of acid - and heat - resistant steel. The scheme of the reactor is presented in Fig. 1.

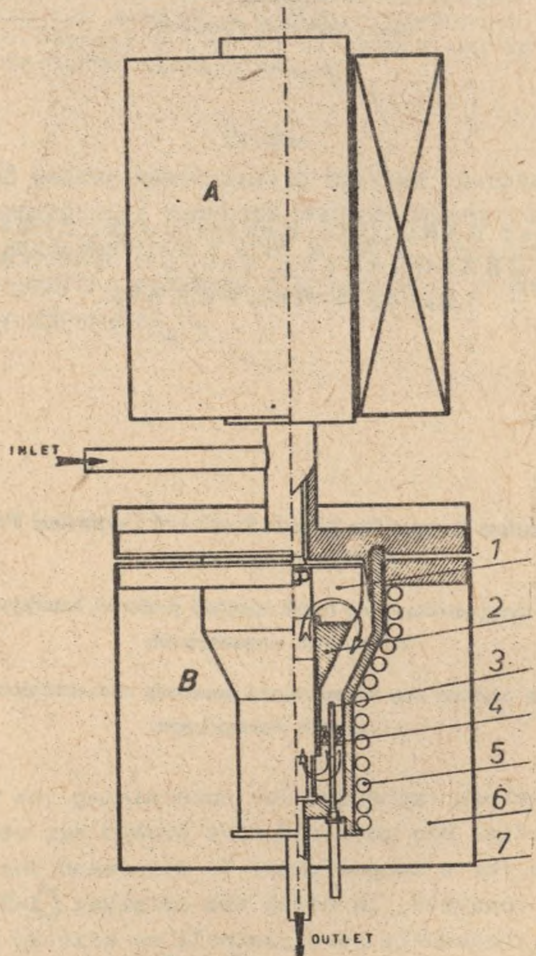

Fig. 1. The scheme of the reactor: A - the power transmission system, B - the head of the reactor, 1 - rotating shaft, 2 - gas nozzle, 3 - thermocouple shield, 4 - catalyst bed, 5 - heating coils, 6 - thermal insulation, 7 - duralism casing

This instrument consists of two parts; the power transmission system denoted by symbol A, and the reactor itself denoted by letter B. The head of the reactor 100 mm in internal diameter has been designed in such a way that on its top wide part the chamber of the rotating shaft is located, in its bottom narrower part a heat-resistant wire net with meshes < 0.1 mm on which catalyst is held. In the middle of the reactor head under the rotating shaft, feed - gas tubes consisting of three parts are located. Its upper part has a conical shape and covers the rotating shaft up. The middle part forms the connecting piece between the conical element and the wire mesh with the catalyst and the lower part, which is affixed to the bottom of the reactor head and equipped with tubes allowing the gas to enter the centre of the agitator. The whole reactor head is placed in a furnace which consists of duralumin casing, asbestos lining and a heating element. The head with the furnace has been fitted to the power transmission part by means of six screws with nuts. Thightness between these elements has been obtained by using a ballistic closing. To impet the reactor a triphaser induction motor with 2870 rpm. 0.6 kVA, has been used. The motor base has been separated from the rotating shaft which has been closed in a pipe connected with the whole instrument. The coiling of the motor base has been cooled with air.

RESULTS AND DISCUSSION

In order to check the gradientlessness of the reactor, some tests were carried out. Temperature distribution was measured inside the reactor chamber in hydrogen and nitrogen atmosphere, in the temperature range 380-850°C. The temperature profile in the vertical axis of the reactor chamber for the temperatures chosen is presented in Fig. 2. It was found that maximal temperature difference in the reaction zone is about -2°C at the very beginning, and then a constant value is obtained on both sides of the wire mesh containing a catalyst. As standard of gradientlessness, a kinetic test was accepted, informing about the change in the reaction rate with that in the geometry of the catalyst bed.

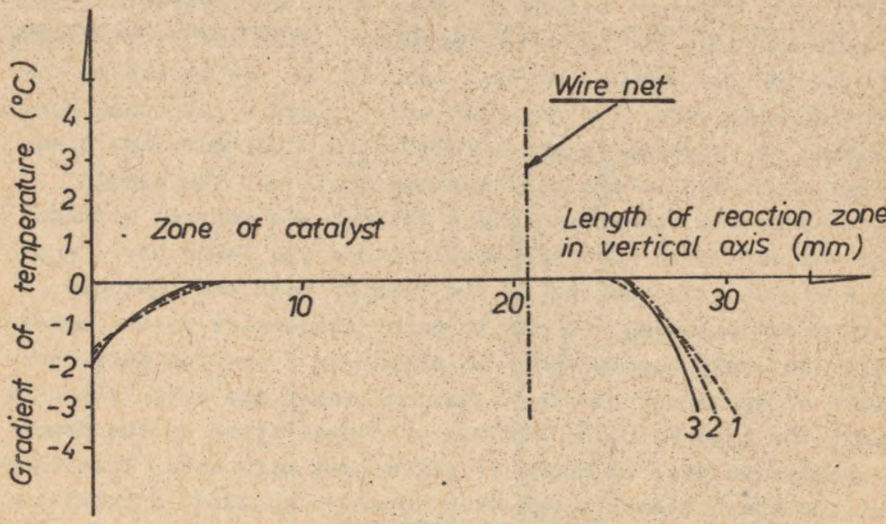

Fig. 2. The temperature profile in the vertical axis of the catalyst bed; 1 - 380°C; 2 - 560°C; 3 - 850°C.

According to the theory, a gradientless reactor should, for a definite catalyst and reaction, at a given temperature and conversion degree, give the same reaction rate regardless of the catalyst weight, i.e. bed geometry. The test were carried out in two reactions: steam reforming of methane and methanation of carbon dioxide. In case of steam reforming of methane, the catalysts were reduced with hydrogen at 850°C for two hrs. Measurements of the reaction rate always started at the highest temperature. The initial ratio of CH_4/H_2O was 1/3. The studies of carbon dioxide methanation were conducted in the temperature range of 300-500°C, at a molar ratio of CO_2/H_2 as 1/4. In both cases the following method was used. Temperature dependences of the reaction rate as a function of the degree of methane or carbon dioxide conversion were measured. From the functions of reaction rate obtained from the degree of methane or carbon dioxide conversion at the given temperatures, temperature dependences of the reaction rate at a constant degree of methane or carbon dioxide conversion were plotted for various catalyst weights. The way of calculating the reaction rate and conversion degree of methane was described in the paper [8]. The reaction products were analyzed chromatographically. For the measurements $Ni/MgAl_2O_4$ catalyst containing 8.6 % wgt of Ni, of total surface 1.4 $m^2/g_{cat.}$, after reduction at 850°C, was used as catalyst. The measurements of reaction rate were performed on 1.2-2.0 mm grains.

From the kinetic measurements carried out it can be seen that the change in the sample from 0.6980 to 2.5026 g does not change temperature dependence of the reaction rate of the methane steam reforming.

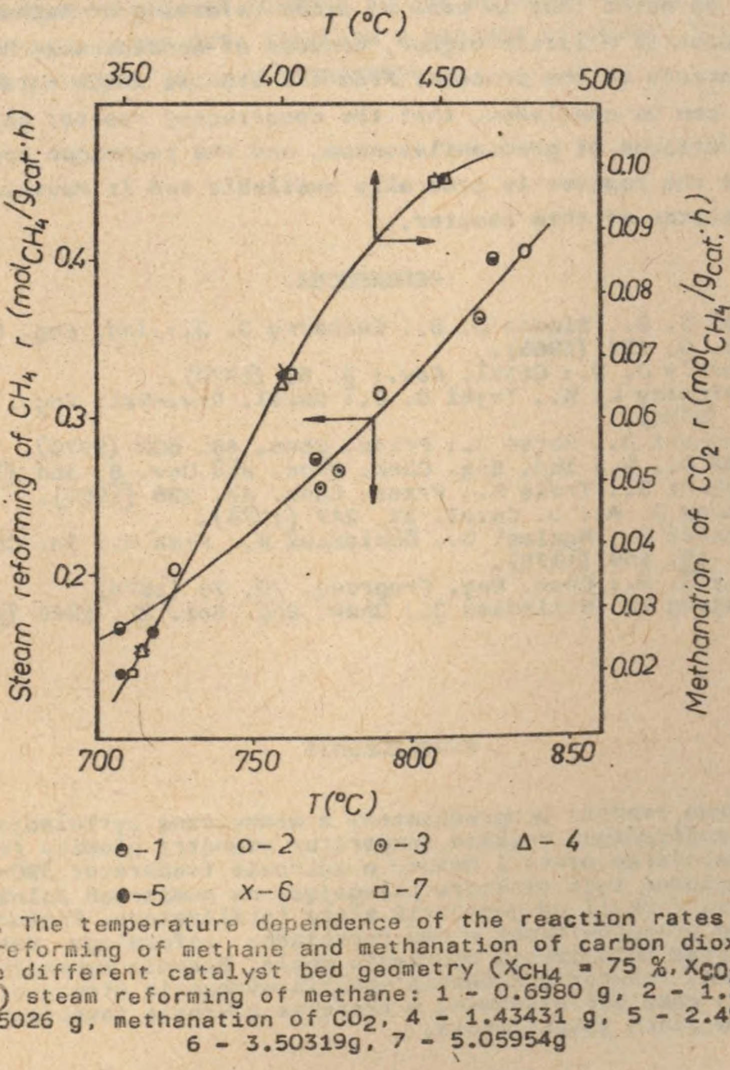

Fig. 3. The temperature dependence of the reaction rates of steam reforming of methane and methanation of carbon dioxide for the different catalyst bed geometry (X_{CH_4} = 75 %, X_{CO_2} = = 65 %) steam reforming of methane: 1 - 0.6980 g, 2 - 1.2233g, 3 - 2.5026 g, methanation of CO_2, 4 - 1.43431 g, 5 - 2.49680g, 6 - 3.50319g, 7 - 5.05954g

An analogical situation was obtained in methanation of carbon dioxide. In this case the changes in the height of the catalyst bed were still higher from 1.43431 to 3,5031 g. Measurements were also carried out in this way that grains of α-Al_2O_3 support of the same size were added, so that the total weight was 5.5954 g, which gave an about 10 mm thick layer of the catalyst bed.

As it appears from Fig. 3, the obtained results show a typical dispersion caused only be inaccuracy in the measurements. It can be noted that in case of steam reforming of methane this dispersion is a little higher, because of considerably higher temperatures of the process. From the studies which were carried out in can be concluded, that the constructed reactor satisfies the conditions of gradientlessness, and the technique applied to test the reactor is generally available and it reveals the possibilites of this reactor.

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STRESZCZENIE

Opisano reaktor bezgradientowy z wewnętrzną cyrkulacją gazów. Przedstawiono rozkład temperatur wewnątrz głowicy reaktora w atmosferze azotu i wodoru w zakresie temperatur 380-850°C.

Opracowano test reaktora polegający na pomiarach zależności szybkości reakcji od geometrii złoża katalizatora. Pomiary kinetyczne przeprowadzono w dwu reakcjach: reformingu parowego metanu oraz metanizacji dwutlenku węgla. Badania wykazały, że opracowany reaktor całkowicie spełnia wymagania stawiane przez teorię i może być stosowany w szerokim zakresie temperatur oraz wymiarów ziarn katalizatora.

Резюме

В данной работе описан безградиентный реактор с внутренней циркуляцией газов. Представлено разложение температур внутри головки реактора в атмосфере азота и водорода в пределе температур 380-850°C. Обработано тест реактора, основанный на измерениях зависимости скорости реакции от геометрии загрузки катализатора. Изменения проводились в двух реакциях: парового реформинга метана и метанирования углекислоты. Исследования показали, что представленный реактор вполне исполняет теоретические требования и может быть применен в широком интервале температур, а также размеров зерен катализатора.

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