PECULIARITIES OF PROPANE DECOMPOSITION INTO NANOFIBROUS CARBON AND HYDROGEN ON NI-CONTAINING CATALYSTS

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Introduction

A number of methods of hydrogen production is known [1]. Nevertheless the most wide used nowadays is hydrocarbon steam conversion. The main process disadvantage is the formation of by-products such as CO and CO_2. And even if the hydrogen is used in fuel cells, the serious problem is to purify the hydrogen from CO, because the carbon oxide is a poison for catalysts used in fuel cells.

To prevent CO formation during the hydrogen production it is suggested to use a process of high-temperature (1200-1800 ^oC) hydrocarbons' pyrolysis [2]. They are proved that the pyrolysis is more efficient way of hydrogen production comparing to the steam reforming owing to the fact that in high temperatures together with hydrogen the structured carbon can be obtained, which costs more than 4000 USD per ton.

But the pyrolysis process has also several shortcomings related to high temperature (such as the need for special materials and high energy losses).

Several years ago it was suggested a new way of CO-free hydrogen and valuable nanofibrous carbonaceous material production, based on catalytic decomposition of hydrocarbon (mostly methane) over Ni and Ni-Cu-containing (up to 90%) catalysts in temperatures of 500-600^oC [3, 4]. The works followed this direction are mostly devoted to the studying the catalytic decomposition of methane [5, 6].

As appears from thermodynamics the only products of hydrocarbons decomposition in relatively low temperatures are C, H_2 and CH_4. And the lower temperature is the lower concentration of hydrogen is obtained. In the temperature of 550 ^oC the concentration of hydrogen is less than 30%. To obtain the higher concentration of hydrogen the methane-hydrogen mixture need to be partitioned and the temperature of the process must be increased.

The effective partition of methane and hydrogen is a large problem. Implementation of methane decomposition in increased temperature is another challenge because of the fast deactivation of catalyst.

This paper explains the possibility to realize the new way of combined obtaining the hydrogen and nanofibrous carbonaceous material through catalytic pyrolysis of propane. Herewith the reaction mixture at the output of reactor consisting of mostly hydrogen and propane.

Results and discussion

Propane decomposition occurred in a perfectly mixed flow reactor with a vibrofluidized bed. Reactor was vertically vibrated with 1 mm amplitude and 10-20 Hz frequency. For all experiments the "pure" propane (98.7 %) with some admixture of C_2 (1.3 vol.%) was used as initial gas.

Heating the catalyst's probe to the predetermined temperature is realized in Ar environment with the following quick switch to C_3H_8. Which is done to know more precisely the time of the reaction start.

The high-percent nickel and copper-nickel catalysts were used.

The analysis of reactor's output hydrocarbons is done chromatographically with the use of Porapak QS column. Measuring of concentration of hydrogen and methane were accomplished with the use of Erba column (zeolite). The calculation of hydrogen concentration was done on the basis of the material balance.

Methane consumption per gram of catalyst varied in the range of 10-100 liter per hour, temperature – within 400-700 ^oC.

The thermodynamics calculation shows that propane converts fully into carbon, hydrogen and methane at the equilibrium conditions.

The experimental studies had demonstrated, that the appropriate catalysts allows us to accomplish the propane decomposition not in equilibrium to carbon, hydrogen and minor quantity of methane, as shown on the Figure 1. It is seen that the yield of products considerably varies during time. First in the period of maximum activity the maximum propane conversion is observed. The methane concentration at this time reaches 20%. After that as the catalyst is being deactivated, the propane conversion slightly decreases. Methane concentration reaches of stable level of 2-3%; concentration of hydrogen decreases but stays at a considerably high level of 60-40%.

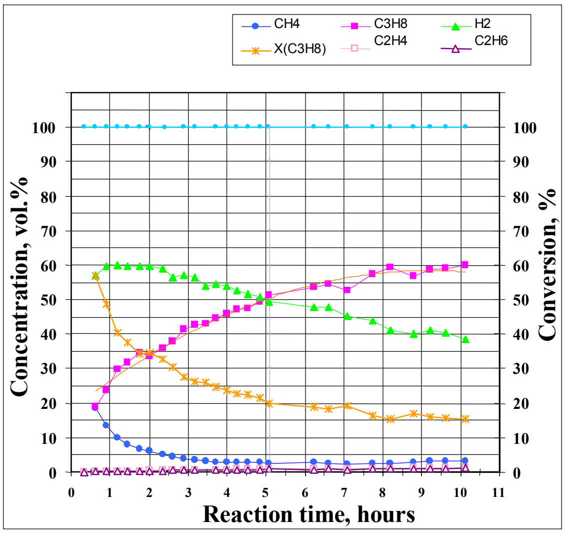

Fig.1. Catalytic pyrolysis of propane:
T=600 °C, gas flow– 100 l/(h*g_{cat})

Obviously, extracting propane out of reaction mixture it is possible to obtain the methane-hydrogen mixture with the hydrogen concentration more than 95%.

Necessary to emphasize that in the process of methane catalytic pyrolysis the similar hydrogen concentration can be obtained in temperatures higher than 850-900 °C only.

Possible expect that the methane formulation is connected mostly with non-catalytic propane conversion in gas phase. To investigate the influence of parallel reactions occurring in the gas phase, series experiments without catalyst was accomplished. The experimental data obtained are shown on the Figure 2. We can see, indeed at the absence of the catalyst in the temperature of 600 °C methane concentration reaches 5%.

Conclusion

The possibility to produce CO-free hydrogen of high concentration on the basic of propane pyrolysis was shown. Efficiency of the process is conditioned by relative lightness of the extraction of propane from reactionary mixture in contrast with methane, for instance, by low-temperature condensation or short-cycle adsorption.

Light-end products of the reaction are hydrogen and unreacted propane which is relatively easy separated from hydrogen, for example, on the basis of methods of low-temperature condensation or short cycle adsorption.

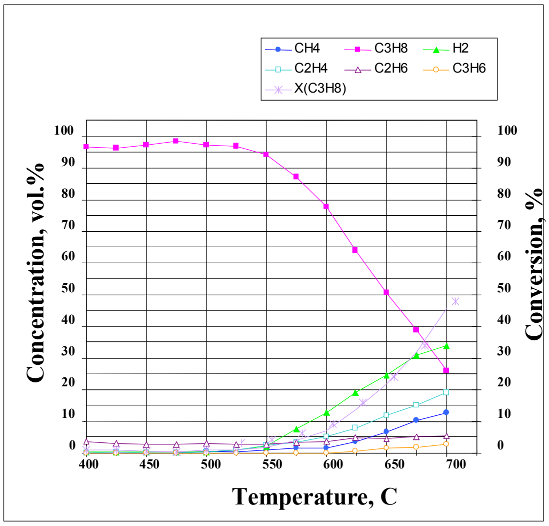

Fig. 2. Non-catalytic pyrolysis of propane.

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