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# Method for Producing Hydrogen and Carbon Nanotubes from Natural Gas

V. V. CHESNOKOV, A. S. CHICHKAN

*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

*E-mail: chesn@catalysis.ru*

## Abstract

A technology for producing hydrogen and carbon nanotubes from natural gas has been developed. The design of a pilot installation was developed and tested in the decomposition of natural gas usinga series of $CoO–MoO_3–Fe_2O_3–Al_2O_3$ catalysts. Theoptimal catalyst composition 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3–Al_2O_3$ was identified. This catalyst makes it possible to obtain 30 L of hydrogen and 12 g of carbon nanotubes from natural gas with 1 g of the catalyst at moderate temperatures (700–750 °C). It was demonstrated that the installation for natural gas processing could operate in a continuous mode with an additional catalyst supply. The concentration of hydrogen in the methane-hydrogen mixture at the reactor outlet reaches 80 vol. %.

**Keywords:** methane, hydrogen, carbon nanotubes, iron

## INTRODUCTION

Hydrogen as a universal highly efficient ecologically safe energy material has a number of indisputable advantages over other energy carriers. First of all, any energy evolution involving hydrogen (fuel element, usual hydrogen heating, hydrogen-fuelled internal combustion engine) results in very favourable energy/mass ratio, that is, hydrogen is a very energy-intensive carrier. It is important that hydrogen is exactly an energy carrier rather than its source. Second, the use of hydrogen is actually free from the emission of hazardous substances: carbon dioxide and methane. Third, hydrogen allows eliminating direct electrification, which is accompanied by high losses during transmission, and there is not possibility to store the energy. Hydrogen allows storing energy and transmitting it over distances [1]. These advantages open enormous outlooks for a broad use of hydrogen in power engineering, especially as fuel for mobile vehicles.

There are several methods to produce hydrogen from different raw material sources [2, 3].

The production of pure hydrogen (99.6–99.99 vol. %) by means of water electrolysis using different electrolyte tanks is a rather well known and studied process [4–6]. This endothermic reaction of water decomposition requires permanent heat supply to the reaction zone. Because of this, electrolysis remains at present the most expensive method of hydrogen production. Nevertheless, electrolysis as a promising method of obtaining hydrogen is of interest for hydrogen engineering because water in comparison with hydrocarbons is a more widespread and almost inexhaustible hydrogen-containing raw material [2].

However, in addition to price, there are also other disadvantages that interfere with a broad propagation of this method. At first glance, this method of hydrogen production should not cause environmental pollution. It should be kept in mind that 63 % of energy in the world is manufactured at heat stations in which fossil fuelsareburnt (gas, oil, coal). So, the negative effect of this method of hydrogen production is transferred tothe stage of manufacturing electric energy.

The oldest method of hydrogen production is coal gasification in the presence of water vapour. The resulting gas contains hydrogen up to 60 % in a mixture with carbon oxide [7]. The major disadvantage of this process is in $CO_2$ emissions, which aresubstantially higher for hydrogen production from coal than for other methods of hydrogen production.

At present, the main industrial method of hydrogen production is the steam conversion of methane (natural gas). According to estimations made by experts, about half of the whole amount of hydrogen produced in the world is manufactured using this method [8–10].

The overall reaction is:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (\Delta H^0 = 173.0 \text{ kJ/mol}) \quad (1)$$

So, 4 moles of hydrogen are formed as a result of an endothermic reaction (1). Theoretical need for energy per mole of hydrogen to provide the entire process is 173.0/4 = 43.3 kJ/mol.

During recent years, works on thermocatalytic decomposition of hydrogen are carried out intensively. The major idea of this method is in the transformationof hydrocarbons into hydrogen and useful carbon-containing substances or materials through their direct pyrolysis [11]. If methane is used as the initial material, the equation for this process will be

$$CH_4 \rightarrow 2H_2 + C \quad (\Delta H^0 = 75.6 \text{ kJ/mol}) \quad (2)$$

One mole of methane gives rise to two moles of hydrogen, and the use of this process is not accompanied by emissions into the atmosphere, while traditional hydrogen production causes extremely severe environmental pollution and the greenhouse regime of the Earth.

Methane decomposition on carbon materials, such as activated coal or carbon black, for the purpose of obtaining hydrogen free from carbon oxides was studied by many researchers [12–17]. Energy consumption for obtaining 1 mole of hydrogen is 37.8 kJ, which is somewhat lower than the value for the steam conversion of methane. Thermal pyrolysis of methane is technologically simple because it is carried out in one stage. In addition to hydrogen, pure carbon, a useful side product, is formed in this process [12]. Capital investment for the creation of hydrogen production through methane pyrolysis is 2.4 times lower than that for the steam conversion of methane [18].

The direct decomposition of methane in comparison with traditional methods of obtaining hydrogen demonstrated very promising results. However, the main problem withthis method is that the yield of carbon per unit mass of the initial coal catalyst does not exceed 60–70 %. Due to this, a great amount of the side product is formed, and it is difficult to find an application for this side product [19]. In addition, due to the low activity of carbon catalysts, the degree of methane transformation is low. Hydrogen concentration at the outlet of the reactor at a temperature of 850–900 °C varies from 32 to 85 % [12–17].

It is known that carbon formation from hydrocarbons on the metals of the iron group proceeds according to the carbide cycle mechanism, and carbon is deposited as nanosized carbon materials [20–22]. Disclosure of this mechanism opens the outlooks for the development of a process of obtaining hydrogen with the formation of carbon nanofibres (CNF) or carbon nanotubes (CNT) instead of the usual carbon black. Many works deal with the development of the method of obtaining hydrogen and CNF from methane [23–27]. In our opinion, a more promising method of obtaining hydrogen from methane is the method in which CNT are obtained along with hydrogen.

Carbon nanotubes are still the object of intense studies because they possess unique electrical, mechanical and physical properties [28–30]. To implement the process of hydrogen and CNT formation from methane or natural gas, it was necessary to develop an active and stable catalyst. It is known that the iron group metals catalyse the growth of carbon nanomaterials. Metal nickel possesses higher activity in methane decomposition than cobalt or iron. However, metal nickel catalyses the growth of CNF, while metal cobalt and iron catalyse the growth of CNT. The growth of CNT proceeds on fine metal particles. For the development of a catalyst for the growth of CNT, it is necessary to use a support that would stabilize the fine particles of metal iron. Results on methane decomposition on cobalt-containing catalysts with the formation of CNT and hydrogen are presented in [31]. However, too low yields of carbon and hence hydrogen were obtained. For this reason, an aluminium-iron catalyst was chosen as the basis. The addition of a small amount of $MoO_3$ (up to 6.5 mass %) to the aluminium-iron catalyst causes an increase in dispersity and modifies the properties of active metal particles due to the formation of Fe–Mo alloy. With an increase in Mo content, the yield of CNT from olefins passes through a maximum. The optimal catalyst is that with the composition 6.5 % $MoO_3$–55 % $Fe_2O_3$–$Al_2O_3$ [32, 33]. A further increase in molybdenum content causes a decrease in the yield because molybdenum is inactive in the process under consideration.

The present work deals with the scientific foundations of the development of the technology of obtaining hydrogen and CNT from natural gas. In particular, the catalyst is chosen, the design of the installation for conducting the process is proposed, and the optimal operation conditions are determined.

## EXPERIMENTAL PROCEDURE

The catalysts were prepared by means of co-precipitation of the nitrates of the corresponding metals. The calculated amount of the salts $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 200 mL of distilled water, and then poured into another vessel together with an ammonia solution maintaining the medium at pH 9. The formed precipitate was kept in the mother solution at room temperature for 30 min, and then washed with a large amount of water to pH 7. In another vessel, the required amounts of $(NH_4)_2MoO_4$ and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 20 mL of distilled water;the solution was added to the formed precipitate, mixed, dried and annealed in a muffle furnace at 350 °C for 30 min, and then at 500 °C for 1 h. The catalysts of the following composition were prepared: 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$ and the catalysts on the basis of 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$, modified with different amounts of cobalt oxide.

Experiments on catalyst carbonization were carried out in a flow quartz reactor. The reactor was equipped with Bac-Ben microbalance, which allowed measuring the changes insample mass directly during reaction and plotting the kinetic dependences. A schematic of the reactor with Mac-Ben microbalance is presented in more detail in [34].

Within the framework of the development of technology for obtaining hydrogen and carbon nanomaterials, a pilot installation with a rotating reactor of continuous action was built [35]. Natural gas decomposition was carried out in the set-up with the flow reactor. The volume of the reactor was 250 $cm^3$. During natural gas decomposition, the reactor was rotating around its axis at the frequency of 1 rpm. The set-up with the rotating reactor for obtaining hydrogen and CNT is shown in Fig. 1.

The catalyst was loaded into the set-up with the rotating reactor. After blowing with argon (30 L/h), the catalyst was reduced for 10 min in the flow of 25 % $H_2$/Ar during heating to 700 °C. Then the flow of a mixture of $H_2$and Ar was stopped, and the flow of natural gas was admitted (7 L/h). The composition of the gas mixture was determined by means of gas chromatography at the inlet and outlet of the reactor.

Methane used in the work has the purity 99.92 vol. %, argon – 99.7 vol %. Natural gas was composed of methane by 97 %, and the rest gases were $C_2$- and $C_3$-alkanes. To purify natural gas from water and sulphur-containing compounds, it was passed through CaA zeolite.

X-ray studies of the samples were carried out with the D-500 diffractometer (Siemens, Germany) with Cu$K_a$ monochromatic radiation (reflected-beam graphite monochromator).

The samples were studied by means of high-resolution transmission electron microscopy

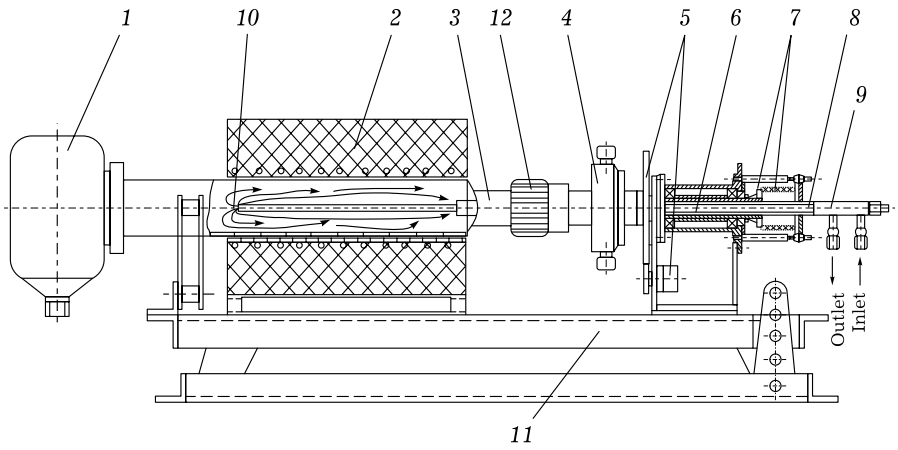


Fig. 1. Schematic of the installation with rotating reactor for obtaining hydrogen and carbon nanotubes: *1* – vessel for the carbon product; *2* – electric furnace; *3* – reactor casing; *4* – charging chamber; *5* – drive (speed-reduction motor, pair of gears); *6* – hollow shaft; *7* – sylphon unit; *8* – tube ($d$ = 10 mm); *9* – tube ($d$ = 16 mm); *10* – thermocouple pocket; *11* – frame; *12* – screw-nut.

(TEM) with a JEM-2010 electron microscope (JEOL, Japan) with the accelerating voltage of 200 kV and resolution 0.14 nm.

## RESULTS AND DISCUSSION

### *Synthesis of catalysts for the decomposition of natural gas into hydrogen and carbon nanotubes*

On the basis of the studies carried out previously, $MoO_3$–$Fe_2O_3$–$Al_2O_3$ catalyst was developed. This catalyst allows obtaining CNT from olefins in a high yield [32, 33]. However, after butadiene replacement by methane, both the rate of carbon nanotube growth and the yield over a 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$ catalyst decrease sharply due to the low reactivity of methane (Fig. 2).

In subsequent studies, having taken the $MoO_3$–$Fe_2O_3$–$Al_2O_3$ catalyst as the basis, we made an attempt to enhance the rate of methane decomposition through the introduction of the second promoting metal into the catalyst. From this point of view, the most promising additive was cobalt oxide (CoO). It is known that metal cobalt is more active than iron in the reaction of carbon formation from methane. So, it was reasonable to assume that the introduction of a small amount of cobalt oxide into the catalyst would cause an increase in the activity of the catalyst in methane decomposition process. A series of catalysts 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$ modified with different amounts of cobalt oxide was prepared and tested in the decomposition of natural gas (Fig. 3).

The dependence of the yield of CNT formed from natural gas over CoO–$MoO_3$–$Fe_2O_3$–$Al_2O_3$ catalysts on the content of cobalt oxide is shown in Fig. 4. Reaction temperature was 700 °C.

Therefore, an optimal catalyst for obtaining CNTfrom natural gas is the 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ catalyst. At a temperature of 700 °C the yield of carbon nanotubes reaches 12 g/g.

### *Morphology of carbon nanotubes*

A TEM image of CNT obtained over the 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ catalyst at a temperature of 700 °C is shown in Fig. 5. The structure of CNT is clearly seen. They are 8–20 nm in diameter.

Replacement of methane by natural gas does not cause changes in the morphology of the formed CNT.

### *Natural gas conversion*

The developed catalyst 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ for natural gas decomposition into hydrogen and CNTwas studied in a large-scale pilot installation with a rotating reactor. The effect of the catalyst amount loaded in the process on the concentration of hydrogen formed in natural gas decomposition is shown in Fig. 6.

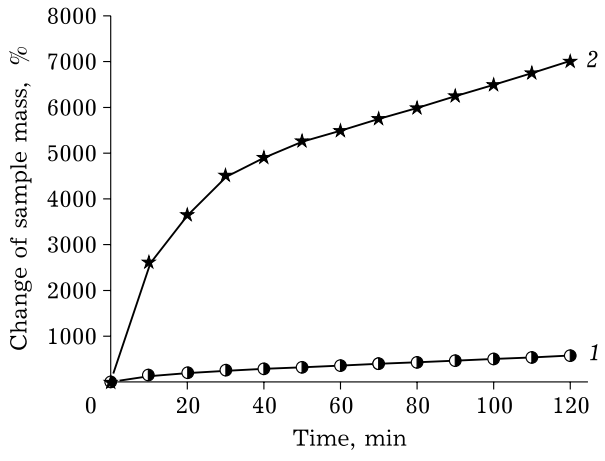


Fig. 2. Kinetic curves of the formation of CNTover 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$catalyst at 700 °C: *1* – from methane diluted with hydrogen (molar ratio $CH_4/H_2$ = 10 : 6); *2* – from butadiene-1,3 diluted with hydrogen (molar ratio $C_4H_6/H_2$ = 1 : 20).

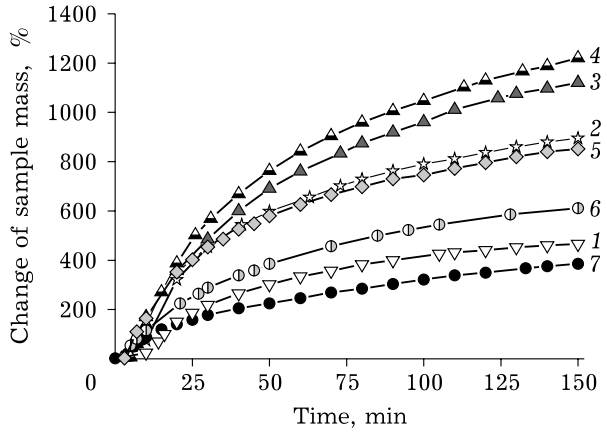


Fig. 3. Kinetic curves of CNTformation from natural gas at 700 °C over 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$catalyst modified with different amounts of CoO: 7 % $MoO_3$–52 % $Fe_2O_3$–$Al_2O_3$ (*1*), 10 % CoO–7 % $MoO_3$–42 % $Fe_2O_3$–$Al_2O_3$ (*2*), 20 % CoO–7 % $MoO_3$–34 % $Fe_2O_3$–$Al_2O_3$ (*3*),30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ (*4*), 40 % CoO–7 % $MoO_3$–16 % $Fe_2O_3$–$Al_2O_3$ (*5*), 45 % CoO–7 % $MoO_3$–15 % $Fe_2O_3$–$Al_2O_3$ (*6*), 58 % CoO–7 % $MoO_3$–$Al_2O_3$ (*7*).

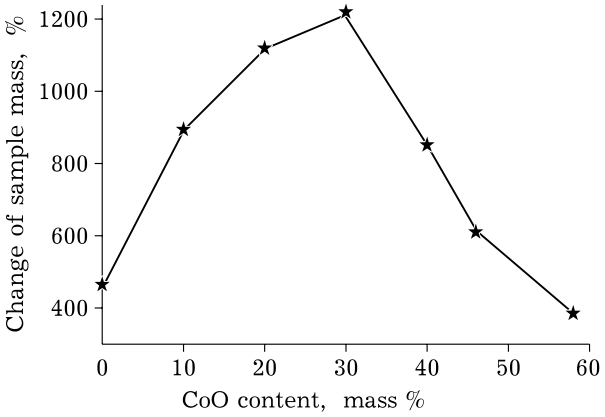


Fig. 4. Dependence of CNT yield from natural gas on CoO–$MoO_3$–$Fe_2O_3$–$Al_2O_3$catalysts on CoO content (700 °C, reaction time 2.5 h).

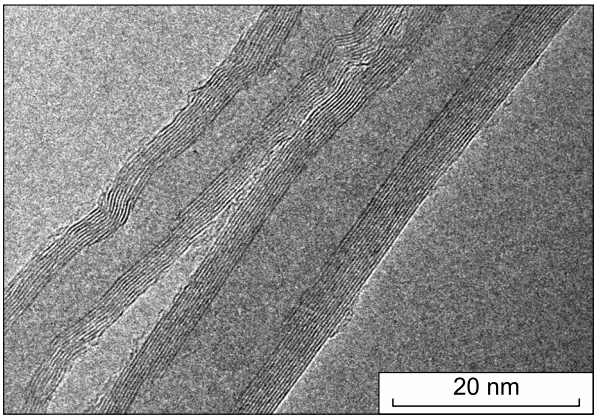


Fig. 5. TEM image of CNT obtained from methane over 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ catalyst at a temperature of 700 °C.

One can see that hydrogen concentration in the products at the outlet of the reactor increases with an increase in the amount of catalyst. The time of the stable catalyst operation increases, too. In the experiments, the catalyst was loaded into the middle zone of the reactor (the angle of slope was 0°), and rotation of the reactor caused only catalyst mixing. In subsequent experiments, the reactor was placed at a small angle of slope (about 4°), so the catalyst was mixed and at the same time displaced along the reactor. Initially, the catalyst (2 g) was loaded into the reactor with the help of a special feeder system. After operation for 4 h, an additional amount of the catalyst (1 g) was supplied to the reactor. Results of the experiment are presented in Fig. 7.

One can see in Fig. 7 that the installation was working in the stable manner for 8 h. Hydrogen concentration in reaction products reached 80 vol. %.

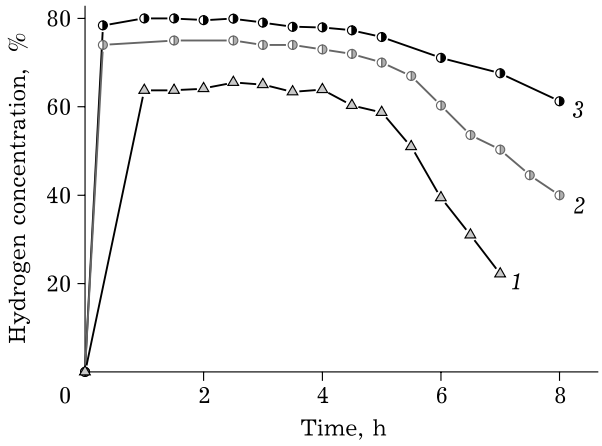


Fig. 6. Effect of catalyst charge on the concentration of hydrogen formed during decomposition of natural gas over 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ catalyst: *1* – 0.5 g; *2* – 1 g; *3* – 2 g. Reaction temperature: 700 °C, the flow rate of natural gas supply: 7 L/h.

## CONCLUSION

The 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$ catalyst was developed, which allowed obtaining 30 L of hydrogen and 12 g of CNT from natural gas using 1 g of the catalyst within the moderate temperature region (700–750 °C).

The obtained catalyst was tested in the decomposition of natural gas into hydrogen and CNT. With an increase in the load, the time of the stable operation of the catalyst and hydrogen concentration at the outlet of the reactor increase. In the installation with rotating reactor, this catalyst allows achieving a 68 % conversion of natural gas. The yield of CNT is 12 g/g. The installa-

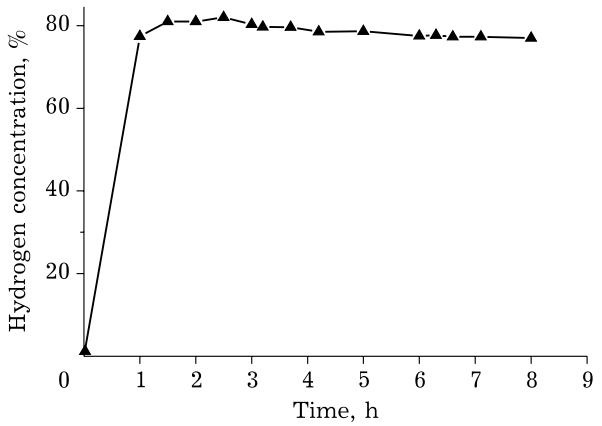


Fig. 7. Dependence of the concentration of hydrogen formed in the decomposition of natural gas over 30 % CoO–7 % $MoO_3$–25 % $Fe_2O_3$–$Al_2O_3$catalyst on time in the continuous set-up operation mode. Reaction temperature: 700 °C, the flow rate of natural gas supply: 7 L/h.

tion may operate in continuous mode with the additional catalyst supply.

Thus, a method for obtaining hydrogen and CNT from natural gas was proposed. From the economic point of view, this method is more favourable than the method of obtaining hydrogen and CNF because the price of CNT is higher than that of CNF.

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