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Low temperature methane coupling in a Pd-based membrane reactor with UV activation

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The nonoxidative coupling of methane to hydrocarbons C_2 and above at 475–555 K by UV activation with hydrogen removing from the reaction zone through a palladium membrane increased CH_4 conversion.

The production of hydrocarbons C_2 and above from methane (methane coupling) is of interest because it allows one to consider natural gas as the alternative source of these compounds for fuel production and chemical synthesis. Because of the very high stability of methane,[1] all the processes with its participation except the oxidation require power expenses.

The basic temporary method to produce hydrocarbons C_2 and above from methane is the thermal activation of CH_4 molecules that breaks a C–H bond. The most obvious way of methane processing allowing such transformations nowadays is the conversion of methane to synthesis gas with the subsequent transformation into desirable products. However, different steps of the process require different conditions, that makes impossible to perform them in one reactor with the use of heat liberating in the reaction. Moreover, the process occurs at 1000–1150 K and higher. For these reasons, the problem of the alternative ways for hydrocarbons production based on methane remains actual.

The example of one-stage process is the oxidative dehydrogenation that may be the result of interactions between methane and oxygen to produce an ethane–ethylene mixture. This process requires a temperature of 950–1150 K and oxide catalysts. Another instance of this process is based on the control of oxygen supplying through an oxygen penetrable membrane to a reaction zone to exclude the deep oxidation of methane.[2,3] Such membranes work with high productivity at 850 K and above.[4]

The energy required for the removal of the first hydrogen atom from the methane molecule is 435.4 kJ mol^{-1}.[1] It corresponds to energy saturation of UV radiation. The use of UV activation allows conducting the process at a low temperature, but the methane conversion remains low because of the reversibility of reactions.

The aim of this work was to study methane coupling in a reactor with a palladium alloy membrane and the activation of CH_4 molecules by UV irradiation.

A mercury lamp and an optical quartz glass reactor were placed on the axises of the elliptical cylinder that was used as the reflector for UV beams. The experiments were performed in the semicontinues regime under atmospheric pressure of pure methane (99.99%) in a temperature range of 480–550 K. Twisted in a screw spiral from Pd alloy with 6 wt% Ru tube with varied length and a wall thickness of 50 μm was placed inside the reactor. The dense alloy structure membranes showed high mechanical strength with permeability for hydrogen only, which was 9% higher than for pure palladium one.[5] The hydrogen formed in the reaction could penetrate through the wall of this tube to its inner volume. Hydrogen formed during the process partially dissolved in the wall of the membrane tube, and, as a rule, in an hour after the experience beginning, in the absence of a stream through a tube, a dynamic balance between sorbed and desorbed hydrogen in reaction zone was established. After 1 h from the beginning of experiment, the argon stream started to pass through a tube, which caused the removal of hydrogen from the reactor in most cases.

The products were analyzed by gas chromatography. Sampling for the analysis was provided every hour. The quantitative analysis of hydrogen concentration in a reaction zone and on the other side of a membrane was not performed because of a small volume of the reactor and, accordingly, a small volume of the formed hydrogen, whose concentration after dilution by argon stream on the other side of a membrane was already insufficient for authentic identification though the hydrogen presence was fixed at the bottom level of sensitivity of the detector.

As expected, the temperature growth leads to an increase in methane conversion (Table 1). The maximum conversion of 14.1% was received at 538 K with the argon flow inside the membrane tube with a length of 1.7 m. The main products of methane transformation were ethane, propane and ethylene. The chromatography–mass spectrometry analysis showed the presence of a very small amount of butane, butene, propane, isopropylenes and trace amount of benzene. The changes of the composition of the reaction mixture in the reactor with a membrane tube 3.8 m in length are shown in Table 2. The conversion increases with the membrane tube length. It allowed reaching the considerable conversion at smaller temperatures due to a rise of a portion of removing hydrogen from a reaction zone.

The growth of an argon flow rate through the membrane tube led to increase in the portion of removing hydrogen from the

Table 1 Effect of temperature on methane conversion in a reactor with a 1 m membrane tube.

Time from the beginning/h	Conversion of methane (%)			
	210 °C	220 °C	240 °C	250 °C
1	1.41	1.83	2.74	3.57
2	4.19	5.62	4.14	5.88
3	5.61	6.90	6.35	8.34
4	6.99	8.97	7.85	9.77
5	8.28	10.69	9.25	10.88
6	9.61	10.20	11.12	11.57

Table 2 Dependence of the reaction mixture composition on the reaction duration.

Time from the beginning/h	Composition (vol%)			
	CH_4	C_2H_4	C_2H_6	C_3H_8
1	99.63	0.11	0.26	0
2	99.55	0.11	0.34	0
3	90.39	0.23	5.13	4.25
4	88.75	0.27	6.44	4.54
5	86.71	0.29	8.03	4.96

reaction zone as well. The influence of an argon flow rate on methane conversion at 523 K is shown in Figure 1. The curve has a maximum in the area with a flow rate of about 40 cm^3 min^{-1}. It is unexpected fact that the replacement of argon by air at a flow rate of 37 cm^3 min^{-1} resulted in lower degree of conversion though hydrogen oxidation, as a rule, leads to growth of the degree of hydrogen extraction from a zone of reaction and to increase in methane conversion. This phenomenon can probably be explained by the interaction between the reaction products and the membrane surface. The adsorbed molecules occupy a part of the surface and decrease the surface area necessary for hydrogen adsorption with further transport through membrane. The similar phenomena were observed earlier[6,7] when full hydrogen removing led to maximum occurrence on the curve of the dehydrogenated substances conversion *vs.* the degree of hydrogen removing.

However, it does not mean that the effect of hydrogen removing does not promote an increase in the conversion of methane. The results of experiments without the Pd tube are shown in Figure 2. The methane conversion after 5 h was at least four times lower than that with a membrane. Moreover, even the presence of a membrane tube without argon flow has provided the conversion growth that may be explained by a partial hydrogen removal.

It is reasonable to assume that the catalytic dehydrogenation of methane on a palladium–ruthenium alloy is possible. However, according to literature data, its probability in the test temperature range is small. The close position of starting points of curves in Figure 2 corresponding to the reactor with a membrane and without it specifies that palladium alloy presence does almost not influence the conversion of methane within the first hour of UV activation.

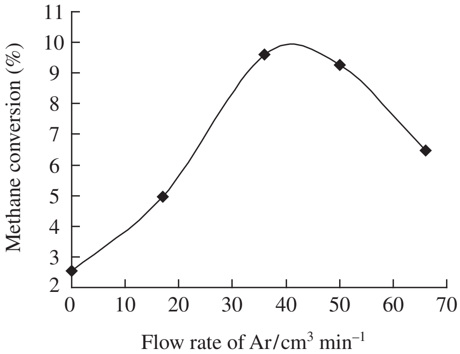

Figure 1 Effect of hydrogen removal with a flow of Ar through a Pd-tube (3.8 m) on methane conversion at 210 °C.

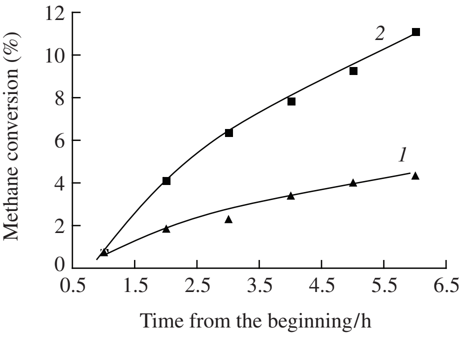

Figure 2 Methane conversion (*1*) without and (*2*) with a Pd-membrane tube.

Rather low temperature not only makes improbable display of catalytic properties of palladium alloy, but also prevents the deep conversion of methane leading to the formation of free carbon, whose traces were not revealed in experiments, neither on a membrane, nor in the reactor. Thus, the UV activation of methane coupling under these conditions allows one to avoid the unproductive expense of methane for the formation of free carbon or carbon oxides that takes place in processes of an oxidative coupling of methane.[3,4]

There are no reasons to assert that observed transformations are the result of photocatalytic processes on a palladium surface that is possible with the use of hard UV irradiation on oxide and metallic catalytic systems.[8,9] All observed transformations are resulted from methane photodissociation under UV radiation. The adding of an ordinary glass screen between the reactor and mercury lamp afforded zero conversion of methane.

The following formation of products *via* methyl radical can be proposed:

$$CH_4 \rightarrow Me^{\bullet} + H^{\bullet}$$
$$2Me^{\bullet} \rightarrow C_2H_6$$
$$Me^{\bullet} + CH_4 \rightarrow C_2H_6 + H^{\bullet}$$
$$Me^{\bullet} + C_2H_6 \rightarrow C_3H_8 + H^{\bullet}$$
$$2H^{\bullet} \rightarrow H_2.$$

Meantime, the presence of ethylene allows us also to assume the formation of carbene:

$$CH_4 \rightarrow {:}CH_2 + H_2$$
$$2\,{:}CH_2 \rightarrow C_2H_4$$
$${:}CH_2 + C_2H_6 \rightarrow C_3H_8.$$

Thus, we demonstrated the occurrence of nonoxidative methane coupling due to UV activation at low temperatures. It allows carrying out the process with smaller power inputs and without the unproductive expense of raw materials. Process performing in the membrane reactor made it possible to increase methane conversion at the expense of formed in reaction hydrogen removing through a palladium membrane. The maximum methane conversion was 14.1% at 538 K.

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