ISSN 1063-7850, Technical Physics Letters, 2017, Vol. 43, No. 5, pp. 460–462. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © V.E. Malanichev, M.V. Malashin, S.I. Moshkunov, S.V. Nebogatkin, V.Yu. Khomich, V.M. Shmelev, 2017, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2017, Vol. 43, No. 10, pp. 12–17.

Studying Barrier-Discharge-Stimulated Plasmachemical Reactions

V. E. Malanichev[a, b]*, **M. V. Malashin**[a], **S. I. Moshkunov**[a],
S. V. Nebogatkin[a], **V. Yu. Khomich**[a], **and V. M. Shmelev**[b]

[a] *Institute of Electrophysics and Electric Power, Russian Academy of Sciences, St. Petersburg, 191186 Russia*
[b] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia*
**e-mail: mve.191@gmail.com*

Received December 22, 2016

Abstract—Barrier-discharge stimulation of chemical reactions has been studied in the case of methane oxidation by atmospheric oxygen with the formation of carbon monoxide and hydrogen. Experiments in a plasmachemical reactor demonstrated the possibility of increasing the yield of synthesis gas (syngas) by means of plasma pretreatment of the initial mixture of air and methane in a 7 : 1 ratio at atmospheric pressure. The output-gas composition was determined by gas chromatography. It is established that the plasma-discharge treatment of the initial gas mixture leads to a 15% increase in the amount of syngas at the reactor output and increases the reaction selectivity with respect to hydrogen and carbon monoxide by 3.2 and 6.5%, respectively.

DOI: 10.1134/S1063785017050224

The synthesis gas (syngas), representing primarily a mixture of carbon monoxide and hydrogen, is used in the commercial synthesis of methanol, hydroformulation reactions, and Fischer–Tropsch process for the production of synthetic fuel and oil [1, 2]. There are several methods of obtaining syngas, including steam reforming of methane, carbonic-acid conversion of methane, partial oxidation of methane by oxygen, and coal gasification. Technologies of syngas production from biomass and municipal solid waste have also been developed [1–5].

Calculations [6] have shown that the cost of syngas accounts for 60–70% of the total cost of methanol and ammonia production and the Fischer–Tropsch process. Thus, decreasing expenditures for the syngas production would have a direct effect on the total cost of these commercial processes.

The present work is devoted to the production of syngas by partial oxidation of methane via the reaction

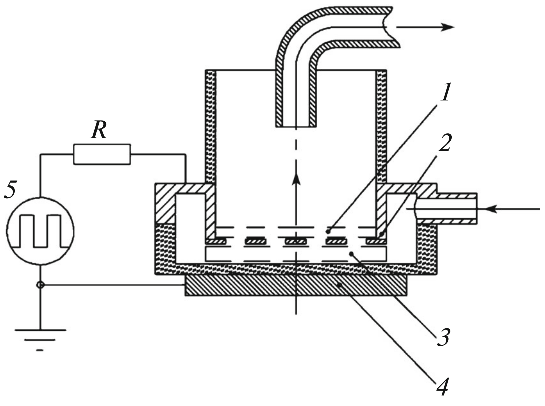
$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2. \qquad (1)$$

Advantages of this method include the exothermal character of the reaction leading to the formation of carbon monoxide and molecular hydrogen in a 1 : 2 ratio (which is necessary for subsequent chemical processes) and the absence of severe corrosion in parts of equipment (which is unavoidable in the case of steam conversion). At present, it is a common practice to increase the efficiency of partial oxidation of methane with the aid of rhodium or platinum catalysts [7–9]. Under these conditions, the selectivity of reaction with respect to hydrogen (S_{H_2}) increases from 25 to 85% and the selectivity with respect to carbon monoxide (S_{CO}) grows from 70 to 96%. A disadvantage of this process consists in the high cost and rapid degradation of catalysts.

Based on some theoretical premises, it can be expected that a certain preliminary treatment of the initial gas mixture can increase the yield and improve the selectivity of syngas production [10]. Indeed, the selectivity with respect to hydrogen and carbon monoxide in various plasmachemical reactors (PCRs) has reached S_{H_2} = 15–60% and S_{CO} = 35–80%, respectively [11–13].

In these experiments, we have used dielectric barrier-discharge (DBD) plasma, which is essentially nonequilibrium. Physicochemical processes in this discharge proceed more effectively than in the equilibrium plasma, since the activation of initial gases is promoted by high-energy electrons. In addition, plasma-pretreated gas in the PCR under consideration did not relax to the initial state and directly entered the reaction zone, because the DBD and combustion regions were located near each other.

The experiments were performed in a PCR with a plane-parallel electrode configuration (see figure), where upper electrode *2* with a 52-mm diameter was made of a steel grid and the lower (grounded) electrode *4* was continuous. The electrodes were separated by a 2-mm-thick dielectric (glass) and 1.5-mm-thick air gap *3*. The reactor was supplied with air–methane in a mixture of 7 : 1 at a total gas-flow rate of 6.9 L/min. The initial gas mixture was pretreated with



Schematic diagram of the experimental setup: (*1*) combustion zone, (*2*) grid electrode, (*3*) discharge gap, (*4*) grounded electrode, (*5*) pulsed high-voltage source, and (*R*) current-limiting resistor.

DBD plasma in region *3* and passed via the grid electrode directly to combustion zone *1*. Combustion was initiated at the reactor output, after which the flame front propagated toward grid electrode *2*, with the subsequent self-sustained combustion taking place near this electrode. The DBD was controlled by applying rectangular high voltage pulses with 10.5-kV amplitude and 60-μs duration at a 4-kHz frequency, which were generated by special source *5* [14, 15].

The chemical composition of the output-gas flow was determined by an M3700 gas chromatograph having three parallel analytic channels, which allowed all components of the gas mixture to be analyzed simultaneously. Accordingly, the chromatograph was equipped with three detectors: one of plasma-ionization type and two of thermal-conductivity type. The chromatographic system included a column packed with CaA molecular sieves, a Porapak Q column, and an HP-PLOT capillary Al_2O_3/KCl column. The output-gas composition was analyzed in three regimes: methane oxidation without DBD plasma pretreatment (regime 1), partial oxidation of methane with DBD plasma pretreatment (regime 2), and partial oxidation of methane in DBD plasma without combustion (regime 3).

The process selectivity with respect to H_2 and CO was calculated by the following formulas:

$$S_{H_2} = \frac{V_{obt.H_2}}{2V_{conv.CH_4}} \times 100,$$

$$S_{CO} = \frac{V_{obt.CO}}{V_{conv.CH_4}} \times 100.$$

where $V_{obt.}$ is the volume of obtained gas (H_2 or CO) and $V_{conv.}$ is the volume of converted methane (CH_4). The reactor was used with a DBD operating in a multichannel mode [16]. The characteristic peak current amplitude was 8 A, the dischargepulse energy was 3 mJ, and the average deposited power deposited in plasma was 25 W.

Results of determination of the output-gas composition and calculation of the reaction selectivity are summarized in the table. Note that the output-gas composition in regime 3 is not indicated, since it was the same as that in the input flow. As can be seen from the data in the table, the amount of CO_2 at the reactor output increases in both regimes increased as compared to the input value, which is indicative of complete oxidation of methane according to the following reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

It should be noted that, when the initial gas was pretreated in DBD plasma, the yield of CO_2 decreased by 0.6 vol %, while the amounts of obtained CO and H_2 increased by 1.8 vol % each. Calculations of the selectivity showed that S_{H_2} and S_{CO} in regime 2 increased by 3.2 and 6.5%, respectively. In view of the above considerations, it can be concluded that pretreatment of the initial gas in DBD plasma leads to an increase in the yield of syngas at the PCR output. This effect is related to activation of the initial gas mixture due to the formation of chemically active particles in the gas.

In concluding, we have studied the barrier-discharge stimulation of chemical reactions in the case of

Results of measurement of the output-gas composition and calculation of the process selectivity

Component/selectivity	Initial gas composition	Regime 1	Regime 2
O_2, vol %	17.5 ± 0.1	2.3 ± 0.4	2.2 ± 0.6
CH_4, vol %	12.3 ± 0.4	0.0	0.0
CO_2, vol %	0.1 ± 0.1	7.3 ± 0.5	6.7 ± 0.3
CO, vol %	0.0	5.2 ± 0.4	6.0 ± 0.4
H_2, vol %	0.0	5.5 ± 0.4	6.3 ± 0.4
S_{H_2}, %	–	22.4 ± 2.4	25.6 ± 2.5
S_{CO}, %	–	42.3 ± 4.7	48.8 ± 4.8

partial oxidation of methane oxidation in a PCR. The process was studied using three regimes, in which (i) the initial gas was pretreated in DBD plasma and immediately passed to the combustion zone, (ii) the gas was not pretreated, and (iii) oxidation took place in plasma without combustion. No yield of syngas was observed in this last case, whereas the combustion of plasma-pretreated gas led to a 15% increase in the yield of syngas as compared to that in the case of a reaction without gas pretreatment in DBD plasma. The selectivity of the plasma-stimulated reaction with respect to hydrogen and carbon monoxide increased by 3.2 and 6.5%, respectively.

Acknowledgments. This study was supported in part by the Russian Foundation for Basic Research, project no. 16-38-60194-mol_a_dk.

REFERENCES

1. S. S. Bharadwaj and L. D. Schmidt, Fuel Proc. Technol. **42**, 109 (1995).
2. C. N. Satterfield, *Heterogeneous Catalysis in Industrial Practice* (McGraw-Hill, New York, 1991).
3. P. F. van den Oosterkamp and R. W. van den Brink, *Encyclopedia of Catalysis: Synthesis Gas Generation-Industrial* (Wiley, New York, 2010).
4. F. G. Rutberg, R. B. Goncharenko, I. I. Kumkova, and A. A. Safronov, Izv. Akad. Nauk, Energet., No. 4, 104 (2015).
5. F. G. Rutberg, A. N. Brattsev, V. A. Kuznetsov, G. V. Nakonechnyi, A. V. Nikonov, V. E. Popov, S. D. Popov, E. O. Serba, D. I. Subbotin, and A. V. Surov, Tech. Phys. Lett. **40**, 725 (2014).
6. J. Haggin, Chem. Eng. News **70** (17), 33 (1992).
7. D. Neumann and G. Veser, AIChE J. **51**, 210 (2005).
8. B. C. Enger, R. Lodeng, and A. Holmen, Appl. Catal., A **346**, 1 (2008).
9. M. Lyubovsky, S. Roychoudhury, and R. LaPierre, Catal. Lett. **99**, 113 (2005).
10. S. Kado, K. Urasaki, Y. Sekine, and K. Fujimoto, Fuel **82**, 1377 (2003).
11. N. Hwang, M. Cha, D. Lee, et al., in *Proceedings of the 6th International Symposium on Non-Thermal Plasma Technology for Pollution Control and Sustainable Energy Development ISNTPT-6, Taiwan, May 12–16, 2008,* p. 95.
12. T. Nozaki, S. Abe, S. Moriyama, et al., Jpn. J. Appl. Phys. **54**, 1 (2015).
13. C. D. Bie, J. Dijk, and A. Bogaerts, J. Phys. Chem. C **119**, 22331 (2015).
14. M. V. Malashin, S. I. Moshkunov, and V. Yu. Khomich, Prikl. Fiz., No. 5, 102 (2010).
15. V. Yu. Khomich, M. V. Malashin, S. I. Moshkunov, et al., IEEE Trans. Plasma Sci. **42**, 3314 (2014).
16. V. Yu. Khomich, V. E. Malanichev, M. V. Malashin, and S. I. Moshkunov, IEEE Trans. Plasma Sci. **44**, 1349 (2016).

Translated by P. Pozdeev