Application of Pulsed Electron Beams in Plasma Chemistry

A.I. Pushkarev, G.E. Remnev

High Voltages Research Institute, av. Lenin 2a, Tomsk, Russia, 634050, e-mail: aipush@mail.ru

Abstract – A review of experimental studies on conversion of gas-phase compounds in the plasma of a pulsed electron beam is presented. An analysis is made of the energy consumption for decomposition of halides (SF_6, WF_6, $SiCl_4$ and $TiCl_4$), pyrolysis and partial oxidation of methane, synthesis of nanosized metal oxide particles and nitric oxides. It is shown that an impact by an electron beam, unlike other plasma formation methods, triggers a chain mechanism of conversion of gas-phase compounds. The electron energy consumption for decomposition of initial molecules is demonstrated to be much lower than the dissociation energy.

1. Introduction

An analysis of the experimental studies on conversion of a variety of chemical compounds by a pulsed electron beam has shown that in many cases the e-beam energy consumption for decomposition of a molecule is much lower than its dissociation energy. The authors interpret the results obtained by the chain character of plasmochemical processes. A chain process involves three stages – initiation, persistence of reaction, and termination of chain. Initiation involves formation of radicals resulting from decomposition of a source product molecule. It requires high activation energy (~3,5 eV/molecule for CH_4), that is to say that the reaction can occur under equilibrium conditions at a considerable rate only at a temperature above 1200 K. Persistence of the chain reaction consists in the interaction of free radicals with initial molecules to form a stable product molecule and a new radical that, in turn, would interact with the initial molecules. This requires a much lower activation energy (0.87 eV/molecule for CH_4), hence a lower temperature for the reaction to occur.

At a temperature lower than 700 K, when no thermal initiation of the reaction takes place, an impact by an electron beam results in a formation of active centers – free radicals, ions or excited molecules – which are capable of initiating a chain reaction. This reaction would occur at a temperature 150-200 degrees lower than that of a conventional thermal process at the same rate, as the plasma action facilitated the most energy-intensive stage – initiation of the reaction. In addition, given a long chain of a chemical process, the electrophysical installation would account only for a small portion of the total energy consumption for conversion of the feedstock. The major energy source in this case is the thermal energy of the initial reacting gas or the energy of exothermal elementary chemical reactions in the chain process (oxidation or polymerization reactions). This significantly reduces the energy consumption for the chemical process. A chemical reaction maintained at a lower-than-equilibrium temperature makes it possible to synthesize compounds unstable at higher temperatures or whose synthesis selectivity at high temperatures is lower. Reduction in the temperature of the chemical synthesis under radiation is similar to a catalytic effect. A chemical process can, however, occur completely in the gas phase, which would significantly increase the reaction rate compared to a heterophase catalytic process. These peculiarities of chain chemical processes under plasma impact appear promising when used in big-volume chemical production.

When analyzing a possible conversion mechanism under plasma action, one has to compare the energy consumption for decomposition of the initial molecules with the energy of their dissociation rather than the thermal effect of the entire process. Under equilibrium conditions, the energy consumption of the first energy-intensive stage of the process – dissociation – is partially compensated for by the thermal effect of the subsequent exothermal reactions. This would result in a considerable decrease in the total energy consumption for the chemical process. Under non-equilibrium conditions, to initiate a chemical reaction it is necessary to deposit energy for decomposition of the initial molecules. The energy of subsequent exothermal reactions would, generally, give rise to increase in the gas temperature, which, at high degree of non-equilibrium under low-temperature conditions, would not give rise to any additional decomposition of the initial molecules.

The purpose of the present work is to study the mechanisms of decomposition of different gas-phase compounds under the action of an electron beam and in a gas discharge on the basis of analysis of energy consumption for the conversion process.

2. Investigation of decomposition of halides

The experimental investigations of decomposition of SF_6 were performed in a specialized pulsed electron accelerator TEA-500 (500 kV, 200 A/cm^2, 60 ns) [1]. It was found out that under pulsed electron beam plasma conditions, decomposition of SF_6 occurs efficiently in a mixture with N_2 [2]. For the mixture

SF_6+N_2+Ar (6:6:1), the electron beam energy consumption for dissociation of one SF_6 molecule was 5 eV, which is lower than that of standard enthalpy formation equal to 12.4 eV/molecule [3]. This is indicative of occurrence of a chain process initiated by the pulsed electron beam. Presented in [4] are the results of experimental investigation of decomposition of SF_6 in a mixture with H_2 under the action of a pulsed electron beam. Figure 1 shows variations in the area of mass spectra peaks corresponding to SF_6, H_2 and sulfur dimer 2S with variations in the absorbed dose of a pulsed electron beam.

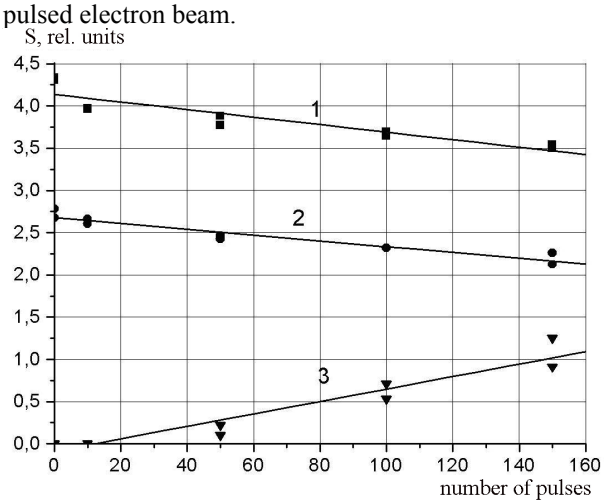

Fig. 1. Dependence of the mass spectra peak area on the number of electron beam pulses: sulfur hexafluoride SF_5^+ (1), H_2^+(2) and sulfur dimer $2S^+$ (3). The peak area values in fig. are multiplied by 20 and those for sulfur dimmer – by 50 times.

The electron beam energy consumption for decomposition of SF_6 was less than 2 eV/molecule. This proves that radiolysis of SF_6 in a mixture with H_2 also follows a chain mechanism.

In [4], the results of an experimental investigation of decomposition of WF_6 in a mixture with nitrogen under the action of a pulsed electron beam at 300 K were presented. The electron energy consumption for decomposition of one molecule of WF_6 was as low as 0.24 eV. The reason for anomalously low energy consumption (much lower than the enthalpy of formation of WF_6 – 17.8 eV [3**Ошибка! Закладка не определена.**]) for reduction of tungsten from WF_6 under a pulsed electron beam is the chain reactions in the plasmochemical process.

An investigation of the processes of decomposition of gas-phase $SiCl_4$ in a mixture with H_2 was performed using a pulsed electron beam of the following parameters: electron energy 300 keV, current density 0.4 kA/cm^2, pulse duration 60 ns. Under the action of this electron beam on the mixture $SiCl_4$+H_2+Ar, there is a loss in $SiCl_4$ and increase in HCl [5] with the increasing number of pulses. In the reactor volume a dark color powder was formed, which acquired white color after letting-to-air [6]. The electron beam energy consumption for dissociation of a molecule of $SiCl_4$ was 1.9 eV (upper estimate not including the electron beam energy lost on ionization and excitation of Ar and H_2). This is much lower than the $SiCl_4$ dissociation energy equal to 6.6 eV. The process of decomposition of $SiCl_4$ under the action of a pulsed electron beam had a number of peculiar features. Heating of the plasmochemical products (the process monitored by pressure variations in the closed reactor) occurred before they reached the temperature much higher than heating by an electron beam only. The reason for low beam energy consumption for decomposition of $SiCl_4$ and considerable heating of the gas is chain reactions in the plasmochemical process accompanied by the energy release.

3. Nonequilibrium synthesis of nanosized oxide powders.

The use of chain plasmochemical processes to synthesize nanosized oxide powders is a new technique to produce powder particles with the grain size less than 100 nm [7]. Nanosized TiO_2 particles were synthesized by injecting a pulsed electron beam (TEA-500) into a gas-phase mixture of $TiCl_4$, O_2 and H_2 [8, 9]. The conversion of $TiCl_4$ was completed after a single electron beam pulse, with the energy consumption for conversion 0.02 eV/molecule. The measurements conducted demonstrated that the gas-phase mixture temperature in the course of the synthesis was as low as 900 K, which is by far lower than that of the synthesis of nanosized TiO_2 particles by other techniques [9]. Shown in Fig. 2 is the dependence of the reactor temperature on time.

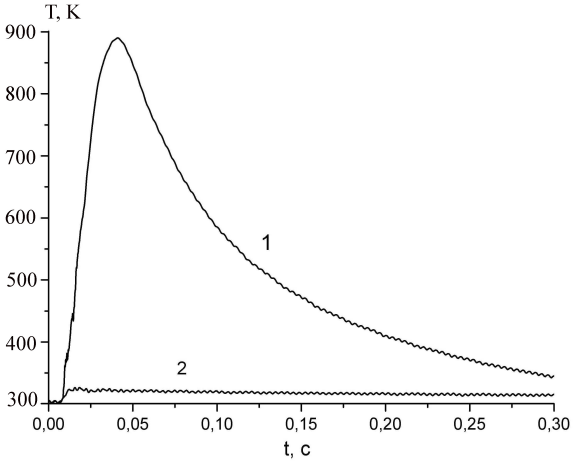

Fig. 2. Temperature variation in the plasmo-chemical reactor: in the course of synthesis of nanosized oxide particles (1) and through heating of the gas mixture by an e-beam (without ignition) (2).

A decrease in the temperature of the synthesis of particles with crystalline structure (rutile and anatase) is due to the non-equilibrium character of the processes occurring in the reactor. The process of destruc-

tion of $TiCl_4$ in a mixture with hydrogen and oxygen under injection of an electron beam was of explosive nature. Alongside the presence of a lower bound of the mixture ignition (with respect to pressure) and the low energy consumption, this is indicative of a chain branching character of the process of TiO_2 synthesis through conversion of $TiCl_4$ in a mixture with oxygen and hydrogen. The resulting oxides have homogeneous composition, and the particles have a characteristic shape with faceting without any inner voids. Measurement of the partial composition of the initial feed allows the crystal structure, shape, and size of the synthesized TiO_2 particles to be controlled.

In order to figure out whether it is possible to simultaneously synthesize nanosized particles of different metal oxides, a series of experiments on excitation of a gas-phase mixture of O_2, H_2, $TiCl_4$ and $SiCl_4$ by a pulsed electron beam [9, 10]. The conditions of synthesis were similar to those in the experiments on synthesis of nanosized TiO_2 particles. The resulting composite powder $(TiO_2)_x(SiO_2)_{1-x}$ had crystalline structure that was well described a composition of two types of lattices typical of TiO_2 (rutile and anatase). Note should be made of a decrease in the average-number size of the composite powder particles less 30 nm) compared to that of pure TiO_2. This is probably associated with the changing conditions of coagulation of the formed particles upon introduction of a new compound. The proposed method of synthesis of nanosized TiO_2 particles and composite nanosized $(TiO_2)_x(SiO_2)_{1-x}$ powder is characterized by low beam energy consumption 0.1-0.15 kW·h/kg of powder. The bulk density of the resulting powder was 6-10 g/l.

4. Plasmochemical conversion of methane

Numerous investigations of decomposition of hydrocarbons under heating demonstrated that the process occurs as a chain reaction (thermal cracking). This reaction of thermal cracking of normal alkanes generally occurs at high temperatures, for instance, for methane at 2500-3000 K.

In [11], the experimental data on plasma pyrolysis of methane are presented. Preheated to 700-1100 K, methane was treated by a pulsed microwave discharge (frequency 9 GHz, power per pulse up to 100 kW, pulse duration 1 μs, and pulse repetition rate 1kHz), which gave rise to a sharp increase in its conversion level. It was shown that this effect could not be interpreted by the thermal action of the discharge, and that the role of plasma consisted in generation of active particles accelerating conversion. The energy consumed by the microwave discharge was 0.9 eV/molecule, which is lower than the C–H bonding energy (4.2 eV). It is worthy of mention that the products of plasma pyrolysis (H_2 and nanosized graphite particles) were essentially different from those of the CH_4 pyrolysis under equilibrium conditions (acetylene, ethylene, and ethane) [12].

In [13], the authors addressed a method to accelerate the methane pyrolysis process by introducing atomic hydrogen into the reacting medium from an arc-plasma source - (voltage 30-70 V, current 50-150 A, power deposited into carrier gas 1.8-2 kW). The reactor pressure was 9.3 kPa. It was shown that at the temperature 2300 K in the discharge region, the chain mechanism accounts for 20 % of the target product. At the temperature corresponding to the discharge periphery (1730 K), the chain mechanisms are also critical. Upon introduction of atomic hydrogen, the total energy consumption for decomposition of methane (for C_2H_n hydrocarbons and nanosized graphite particles) decreased (with respect to conversion) from 15 to 11 eV/molecule. During pyrolysis, the energy consumption in the region of high temperatures was 15 eV/molecule in both cases.

In [14], the results of methane pyrolysis under a pulsed electron beam (TEA-500) at 300 K are discussed. The major pyrolysis products were ethylene and acetylene. Given that the total electron beam energy is consumed by the decomposition of methane and by the conversion products – acetylene and ethylene - the electron beam energy consumed by the former was 120±5 eV/molecule. It was, however, experimentally found out that the beam energy absorbed by the gas was as low as 15 % [15], the energy consumed by the e-beam was, therefore, 18±2 eV/molecule of methane.

The investigations of methane pyrolysis in plasma demonstrated that in order to initiate a chain process of plasma pyrolysis of methane, a certain optimum gas temperature is required, which would ensure an effective chain evolution.

Oxidation of hydrocarbons is also a chain degenerate-branched process. An examination of hydrocarbon oxidation at low pressure demonstrated that facilitation of initiation by an external action allows oxidation to occur at low temperatures, down to room temperature [16, 17]. The main product of this low-temperature oxidation is the alkylhydroperoxide. A small length of the chain under these conditions, however, makes this low-temperature oxidation of hydrocarbons less efficient as concerns the yields of the resulting products and the conversion level.

In [18, 19] partial oxidation of CH_4 in a pulsed microwave discharge (streamer, pseudo-corona discharge: $\lambda = 3$ cm, pulse power 300 kW, average power up to 300 W, pulse duration 1 μs, and pulse repetition rate 1 kHz) and in a continuous microwave discharge (coaxial flare discharge: frequency 2.45 GHz, and power 1-5 kW). The initial reaction agents were heated to 800…1200 K and fed to a discharge chamber integrated with the zone of CH_4 combustion. The authors noted that the microwave discharge used exerts a two-fold action on the system. On the one hand, it effectively facilitates the input of thermal energy

even into highly heated reaction agents, due to high temperature of the plasma. On the other hand, plasma generates active particles favoring oxidation of CH_4 in chain reactions and acts as an initiator of combustion. For the reaction of partial oxidation of CH_4, the energy input from the microwave discharge was 0.25 eV/molecule with the conversion level 70 %, they increased to up to 0.5 eV/molecule when the conversion level tended to 100 %.

In [14, 20], the results of experimental investigation of CH_4 oxidation under a pulsed electron beam (TEA-500) are presented. With electron beam acting on a mixture of CH_4, O_2 and H_2 (cumulative pressure 50-70 kPa, temperature 300 K), a chain regime of partial CH_4 oxidation was initiated. The process of partial oxidation of methane was effectively maintained at a high oxygen concentration (over 30 %) in the initial mixture. Figure 3 depicts the dependences of the mass spectra peak area of main products of methane decomposition on the initial CH_4 pressure.

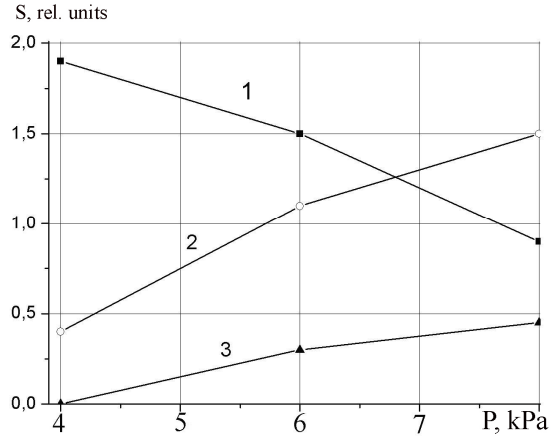

Fig. 3. Dependence of the mass spectra peak area of the gas mixture upon treatment by an e-beam on the initial methane pressure: CO_2^+ (1), CO^+ (2), and H_2^+ (3). The hydrogen peak area is multiplied by 10.

The electron beam energy consumption for CH_4 conversion did not exceed 0.05 eV/molecule. Decomposition of CH_4 by an electron beam was totally completed within one pulse.

In [21], the results of investigation of methane decomposition in a mixture with water in the gliding discharge plasma are reported. The experiments were performed at the mixture temperature 450 K and atmospheric pressure. The discharge power was 1 kW, frequency – 50 Hz, gas mixture feed rate – 30 l/m. For the ratio CH_4/H_2O = 0.67, the conversion level reached was 50 %. The main conversion products were H_2 (55 %) and CO (10 %), with the relative energy consumption for decomposition of CH_4 being 0.92 eV/molecule. The energy consumption for vapor conversion of methane in the gliding discharge plasma as low as that are indicative of the chain character of the process.

Numerical kinetic analysis of plasmochemical reactions initiated in a low-temperature plasma of gas discharge in the CH_2+O_2 mixture of atmospheric pressure has been done based on a compatible model by the authors of [22]. The chain mechanism of radical formation in the ion-molecular processes with the assistance of water and oxygen molecules was considered. The mechanism allows considerably decreasing energy consumption for generation of oxidation products.

5. Plasmochemical synthesis of nitric oxides

In addition to its significant applied value, oxidation of atmospheric nitrogen in plasma is appealing due to the fact that it could be effectively stimulated by vibrational excitation of the reacting molecules. The experimental investigation of the NO synthesis in nonequilibrium plasma had been done since 1930s in a gliding discharge. The energy consumption for nitrogen synthesis in those systems remained quite high. Low values of energy (7 eV/molecule of NO) were obtained at atmospheric pressure in semi-self-maintained discharges sustained by high-current electron beams. The lowest energy inputs of ~3 eV/molecule were achieved in a non-equilibrium microwave discharge with a magnetic field operating under an electron-cyclotron resonance [23].

It was shown in [23] that synthesis of nitric oxides from a mixture of nitrogen and oxygen may occur as a chain process under the condition of vibrational excitation of nitrogen molecules. The work reports the sequence of the chain oxidation process.It was noted that the value of energy consumption for nitrogen oxide synthesis obtained experimentally with glow, spark, and beam discharges was 30-100 g/(kW·h) or 3.3-11 eV/molecule at the nitrogen concentration less than 1 %.

Presented in [24] are the results of investigations nitric oxide synthesis in plasma formed by a high current pulsed electron beam (TEA-500) and estimations of the energy consumption for nitrogen conversion. The experiment made use of a mixture of gases H_2+O_2+N_2 at atmospheric pressure, and the mixture temperature was 300 K. This experimental research demonstrated that under a pulsed electron beam a chain regime of partial nitrogen oxidation is developed. The end reaction products are nitrogen oxides NO and N_2O. No nitrogen dioxide NO_2 was detected in the reaction products. The energy input for nitrogen oxidation was found to be 0.11 eV/molecule, which is much lower than the values in the other processes for nitric oxide synthesis.

Summary

The review of the experimental works on gas-phase plasmochemical processes has demonstrated that the

conditions developed under the action of a pulsed electron beam on gas are favorable for initiation of chain chemical processes. In contrast to other plasma formation techniques, a high-current pulsed electron beam provides a considerable reduction in the energy of electrophysical installation for completing the chemical reaction, which is a critical factor in the case of limited power supply. Under non-equilibrium conditions generated by a pulsed electron beam, no inhibiting effect of high oxygen concentration on partial methane oxidation is manifested. Unlike other techniques, a pulsed electron beam irradiation helps synthesize nanosized titanium dioxide particles with crystal structure at low temperature. A considerable reduction in the temperature threshold of particle crystal structure formation has also been achieved for composite nanosized particles of $(TiO_2)_x(SiO_2)_{1-x}$ oxides.

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