STUDY OF PROCESSES IN N₂/CH₄ ACTIVE DISCHARGE
AND IN FLOWING AFTERGLOW CONDITIONS

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Abstract

In the contribution the first results of the comparative study of
chemical processes in N₂/CH₄ plasma generated by various types of
discharges are presented. As a method of solution of this task a
computer experiment was chosen. For the present moment most
results were obtained in the flowing afterglow conditions.

1. Introduction

The conversion of methane in more suitable products is always a challenge for
petroleum industries and for research groups in laboratories of chemistry. New environmental
concerns have added to commercial interest in methane conversion. To initiate this
transformation it is necessary to break the strong c-h bond. This can be achieved either by
classical methods as thermal coupling, direct oxidation and catalytic oxidative coupling or by
various types of electrical discharges.

One of the most important tasks of methane plasma chemistry is the production of
polymer, hydrogenated amorphous carbon and crystal diamond films as well as preparation of
higher hydrocarbons from natural gas, detoxification of gases generated by combustion, study
of chemistry of atmospheres of large planets and their satellites, etc. The kinetics of methane
decomposition in various plasma mixtures, especially in N₂/CH₄, H₂/CH₄ and Ar/CH₄ discharges,
has been studied from the first half of last century.

There exist various experimental techniques used for the decomposition of methane into
simpler hydrocarbons by means of plasma. These techniques can be divided into two basic
groups:
- Processing in active discharges (radio-frequency, electron-cyclotron resonance, dc,
microwave).
- Processing in flowing afterglow.

While the first group of discharges can lead even to complete dissociation of hydrocarbons
and, if desired, to preparation of solid products, the afterglow conditions with lower energies
are much more convenient for efficient gaseous chemistry.
Besides purely experimental approach the hybrid methodology, i.e. the combination of
direct measurement and computer simulation, proved to be a very convenient tool for the
study of processes in gaseous chemistry of methane. Such technique is typically used for the
analysis of complex problems, physical and chemical processes in methane plasmas being one
of them.

The aim of our work is to give an insight into the basic mechanisms leading to
decomposition of methane and preparation of both solid and gaseous stable products in
various experimental conditions. The understanding of physical and chemical mechanisms is
necessary for the optimisation of plasma-chemical technologies. Therefore, a computer
experiment describing the N₂/CH₄ plasma was prepared and with its help both the common
features and differences of methane decomposition in active discharges and in afterglow
conditions will be studied in future. In this contribution the first results are presented.

2. Active discharges

The decomposition of methane in active discharges in both pure methane and its
mixtures with other gases is one of the typical plasma-chemical technologies – e.g. [1], [2].
For the discussion of experimental data and optimisation of technological processes,
especially in the direction of diamond-like thin film growth, many models of methane
conversion and carbon containing thin films deposition were suggested. These models are
focused on given plasma technologies – e.g. on radio-frequency glow discharges in pure
methane [3], on dc glow discharge in nitrogen-methane mixtures [4] or on microwave
discharge in hydrogen-methane gas mixtures [5].

From the discussion of experimental data based on these models the conclusion can be
derived, that the decomposition of methane in active glow discharges is very effective,
especially for low relative concentrations of methane, and that the final (non-stable) products
are typically lower hydrocarbon radicals and carbon atoms resulting often in solid films.
However, when the N₂/CH₄ gas mixture is used, non-negligible number of carbon atoms will
be intercepted in nitrogen-containing species, especially HCN, both gaseous and solid. From
all mentioned models it followed that the role of charged species in very important in active
discharges, although the excited species must be taken into account, too. Further, when
discussing CVD growth processes, the complete models must consist both from gas-phase
chemical processes and surface chemical processes.

3. Flowing afterglow conditions

The processing in the flowing afterglow conditions, especially when mixing methane
into the afterglow of some other gas – e.g. N₂, leads to slightly different gaseous chemistry of
methane. Its advantage is, that it is possible to obtain simultaneously high active species for
the initiation of the methane decomposition and ground state particles for the rapid
stabilisation of obtained products. These conditions are favourable to the production of
gaseous products [6], contrary to active discharges that are mostly used for the cvd production
of solid films. However, sometimes the effective conversion of methane into higher gaseous
hydrocarbons can be done also in active discharges [7].

The physical and chemical processes in the N₂/CH₄ flowing afterglow were studied by
the combination of direct measurement and computer modelling e.g. In [6], [8]. In our
experimental conditions, when the methane was mixed with activated nitrogen downstream
the discharge reactor, it was found that, contrary to active discharges, the role of charged
particles is unsubstantial compared to excited species both during the initialisation of methane decomposition and during further conversions to stable products. The c2 hydrocarbons were found (especially c2h2, c2h6, and c2h4) the main stable species, while the production of solid products was negligible. It was found too, that the influence of chemical reactions with nitrogen is significant, the most important product being the gaseous hcn.

3. Computer experiment

in order to compare mechanisms in gaseous methane chemistry under different discharge conditions a computer experiment was prepared. The technique of simulation for both groups of discharges was the same: models consisted of reactions between neutral, charged and excited species – electrons, hydrocarbons, radicals, nitrogen containing species, hydrogen and nitrogen. The rate constants of these reactions depended on experimental conditions – electron and gas temperature, etc. Further influence of experimental conditions was included into spatial concentrations of some species. These data were derived from probe measurements and emission-optical spectroscopy. For the solution of models a macroscopic kinetic approach was used – the concentrations of individual species were derived as a solution of ordinary differential equations based on balance equations for these species.

the model of active discharges is based both on results from the literature and on our model [9]. For the present moment our model consists of 285 reactions between 70 species. The complete model consists of two submodels – model of processes in pure n2 plasma and model of n2/ch4 plasma, into which the simplified model of n2 plasma was included. For the solution of the complete model the technique of kinetic scheme reduction [10], [9] must be used, as the resulting set of equations is too stiff.

During the study of processes in the flowing afterglow conditions several computer models of increasing complexity were prepared – ranging from 61 chemical reactions between 24 most important species [6] to present model of methane decomposition in nitrogen microwave afterglow created by 166 reactions between 46 species. For the numerical solution of so large and complex model the reduction technique must be used, too.

4. Results and discussion

till now most results were derived for the n2/ch4 microwave afterglow. The results obtained before (e.g. [6], [8], [10]) and our present calculations can be summed up:

- **Mechanism of dissociation:**
  
The main channel for the initial decomposition of ch4 molecules is the excited molecular nitrogen ( n2(a) and n2(a'), while the role of electrons and ions is completely negligible and the role of excited atomic nitrogen is small enough (it was estimated to be below 1 %).

- **Stable products:**
  
The final stage of methane conversion in the flowing afterglow conditions found to be following stable products: c2h2, c2h4, c2h6, h2 and hcn, plus small amounts of higher hydrocarbons (c3h8, c4h10, ...) And further nitrogen containing products.

- **Kinetic scheme:**
The computational method used enabled to construct the kinetic scheme of methane conversion. The kinetic scheme of the complete set of 46 species it too complicated and cannot be expressed graphically. However, with the help of method of reduction it is possible to derive simplified schemas for the important stable products – an example is shown in fig. 1.

![Kinetic scheme in simplified model of methane decomposition](image)

Fig. 1: kinetic scheme in simplified model of methane decomposition
In the flowing afterglow conditions.

Flows of carbon atoms:
With the help of computer experiment it is possible to study in detail flows of c, h and n atoms during the methane conversion to stable products. In the flowing afterglow conditions the reactivity of plasma is time-dependent and decreases very profoundly with the distance from the microwave discharge. For the smaller model (61 reactions between 24 species) it was demonstrated in [11], that in the beginning nearly all carbon atoms are bound with the nitrogen into hcn and other nitrogen containing species through the reaction channel: \( \text{ch}_4 \rightarrow \text{ch}_3 \rightarrow \text{hcn} \) (see fig. 1). The situation is changed dramatically after several milliseconds of the afterglow time, the above mentioned reaction channel will be blocked and instead of it channels to higher hydrocarbons will be opened: \( \text{ch}_4 \rightarrow \text{ch}_3 \rightarrow \text{c} \rightarrow \text{h}_2 \rightarrow \text{c}_2 \rightarrow \text{h}_4 \rightarrow \text{c}_3 \rightarrow \text{c}_2 \rightarrow \text{h}_6 \), etc. With the help of large afterglow model similar analysis can be performed with nearly identical results, only the reaction channels are more complicated.

In active discharges the situation is quite different. Here the most important mechanism of initiation of the methane decomposition is the interaction with electrons (in afterglow conditions this mechanism is not important due to extremely rapid decay of both electron concentration and energies). Other mechanisms take part in the initiation process.
too and their weights differ for various types of active discharges, however all these additional mechanisms constitute minor reaction channels only. The kinetic scheme of the active glow discharge in the \( \text{N}_2/\text{CH}_4 \) mixture is much more complicated because besides reactions between radicals the reactions with charged species becoming important too. Moreover, when studying the hydrogenated carbon film growth, the processes caused by accelerated ions bombarding the growing layer must be taken into account.

Our model of the \( \text{N}_2/\text{CH}_4 \) plasma [9], which we are preparing in order to describe the influence of concrete experimental conditions and to discuss the probabilities of individual reactions channel leading either to solid layers or to gaseous higher hydrocarbons, is not able to give yet quantitative results. The work in this direction will be continued in future.

REFERENCES


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