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PLASMA PROCESSES FOR THE ENVIRONMENT PROTECTION

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A b s t r a c t. The search for effective methods of preventing environment degradation draws attention to plasma technologies: pyrolysis of stable an gaseous materials, vitrification of waste materials, gasification of organic waste, cleaning exhaust fumes. Modern plasma technologies offer many solutions that may be applied for these purposes.

K e y w o r d s: plasma, pollutant decomposition, environment protection.

INTRODUCTION

The development of industry, communication and transport networks, the power consumption increase and rapid growth of urban areas have become, in the last century, a source of quite new problems, that arise along with the rapidly progressing devastation of the environment including earth, surface and ground waters, and atmospheric air. The management of these problems have been started with too much a delay relative to the period of their growth but, fortunately, nowadays the environment protection have become one of the fundamental elements imposing the development strategy of our civilisation. These problems have given rise to creation of a new domain of technology aiming to prevent the environment degradation and to restore the devastated areas to a state reminding, as much as possible, their original form.

In the search for effective methods for preventing environment degradation attention has been drawn to plasma technologies. In several fields the electroplasma processes have shown some substantial advantages relating to the other methods. These are:

- The pyrolysis of stable materials, especially of toxic substances which are not decomposed under normally applied incineration conditions. As generally known, such combustion processes can give rise to formation of dioxins, furans or other stable chloroorganic compounds. The problem is concerned with both current industrial wastes and the disposal of overdue or retired chemical products, such as e.g. biologically active substances.

- The vitrification of waste materials containing considerable amounts of toxic components, e.g. heavy metals, occurring in stockyards in chemical forms enabling their propagation and pollution of the environment along with the rain waters.
- Gasification of waste organic materials (e.g. polymers) that can not be effectively recycled.
- Removal of acid oxides (NO_x i SO_x) and other noxious components of the flue-gas (CO, hydrocarbons) from the power plants and car engines.
- Conversion of toxic substances occurring in industrial waste gases, often highly diluted with inert components.
- Processing of some stable substances occurring as industrial side products or retired from the technological use because of some harmful properties, e.g. fluoroorganic compounds, nitrous oxide.

The modern plasma technologies have been offering many solutions that are (or may be) applied for the above purposes. Plasma-jet and arc reactors are often used for high-temperature processing of stable waste materials (pyrolysis or gasification) and for the vitrification. Corona discharges, particularly when generated in the pulse mode, can be used effectively for cleaning power station flue-gas and of some waste industrial gases. A high efficiency in transformation of some volatile substances of rather low chemical activity can be attained using gliding discharges (Glid-Arc).The above example are far of exhausting all the variants being investigated. In particular, methods coupling the chemical action of plasma with heterogeneous catalysis seem to be worth of much interest.

CHEMICAL REACTIONS IN NON-EQUILIBRIUM PLASMAS

Despite of a great number of studies performed, the reaction kinetics under plasma conditions still remains insufficiently known because of complexity of these processes. It concerns, in particular, the non-equilibrium plasmas, where short-lived components of high activity, (excited molecules and active free radicals) are of primary importance. Some processes, examined in recent years, may be taken as examples. One of them [1] is concerned with NO and SO_2 removal using ammonia in the complex gas mixture $NO+SO_2+CO_2+N_2+O_2$ in corona discharges (Table 1). In this process, an essential the role of free radical OH has been found, as it initiates many reactions with other, more stable reactants. It is generally known, that the presence of water vapour accelerates many reactions effected in the medium of plasma. This fact is mainly due to the formation of OH radicals (Table 2) [2]. On the other hand, singlet metastable states of nitrogen molecules are responsible for the NO destruction in N_2+NO mixtures [3]. A complex mechanism is also observed in the plasma processing of simple

chloroorganic compounds CCl_4 and CH_2Cl_2 in air (Table 3) [4]. The active species participating in this process are the atoms of nitrogen and oxygen. These and many other examples [5] confirm the fact that the occurrence of active, unstable intermediate products is characteristic for the reactions proceeding in non-equilibrium plasmas and it has a substantial bearing on their kinetics (Fig. 1).

Table 1. Reactions of NO and SO_2 with ammonia in gas mixture $NO+SO_2+CO_2+N_2+O_2$ under corona discharge conditions [1].

FAST:	OTHER:	
$NO + NH = N_2 + OH$	$NO + H + H = HNO + H$	$SO_2 + O + M = SO_3 + M$
$NO + NH_2 = N_2 + H_2O$	$NO + OH + N_2 = HNO_2 + N_2$	$SO_3 + H_2O = H_2SO_4$
$NO + N^* = N_2 + O$	$NO + H^- = HNO + e$	$2SO_2 + 4OH = 2\,H_2SO_4$
$NO_2 + N^* = N_2 + O_2$	$NO_2 + OH + N_2 = HNO_3 + N_2$	$H_2SO_4 + 2NH_3 = (NH_4)_2SO_{4(S)}$
	$NO_2 + HO_2 + N_2 = HNO_3 + N_2 + O$	$3SO_2 + 3NH_3 = (NH_4)_2S_2O_5 + HNSO$
	$HNO_3 + NH_3 = NH_4NO_3$	

Table 2. Reactions of H_2O in mixture of 5% O_2, 10 % H_2O, 15 % CO_2 and 70 % N_2 in discharges or in electron beam [2].

$e + H_2O = H^- + OH$	$N_2^+ + O_2 = N_2 + O_2^+$
$e + H_2O = e + H + OH$	$O_2^+ + H_2O + M = O_2^+(H_2O) + M$
$O(^1D) + H_2O = 2OH$	$O_2^+(H_2O) + H_2O = H_3O^+ + O_2 + OH$
$e + O_2 = 2e + O + O^+$	$O_2^+(H_2O) + H_2O = H_3O^+(OH) + O_2$
	$H_3\,O^+(OH) + H_2 = H_3O^+ + H_2O + OH$

Table 3. Reactions of CCl_4 and CH_2Cl_2 in corona discharges or in electron beam [4].

$e + CCl_4 = CCl_3 + Cl^-$	$e + CH_2Cl_2 =$ products
$CCl_3 + O_2 + M = CCl_3O_2 + M$	$O + CH_2Cl_2 = OH + CHCl_2$
$CCl_3O_2 + Cl = CCl_3O + ClO$	$N + CH_2Cl_2 = NH + CHCl_2$
$CCl_3O = COCl_2 + Cl$	$N + CHCl_2 = 2Cl + HCN$
$ClO + O = Cl + O_2$	$2CHCl_2 = (CHCl_2)_2$
$2Cl + M = Cl_2 + M$	$(CHCl_2)_2 + Cl = HCl + CHCl_2CCl_2$
$CCl_3 + O = COCl_2 + Cl$	
$CCl_3 + N = ClCN + 2Cl$	
$COCl_2 + O = ClO + COCl$	
$COCl + M = CO + Cl + M$	
$COCl + O = CO_2 + Cl$	

NEW TECHNIQUES FOR NON-EQUILIBRIUM PLASMA PROCESSING

Some electroplasma processes for the removal of NO_x and SO_x from flue-gas have been applied in some power plants. The highest efficiency has been observed in the case of corona discharges in pulsed systems and in processes provoked by a high energy electron beam generated in accelerators [6]. Such processes have been applied in commercial or pilot plant scales. For example, a 0.5 MW reactor for the removal of NO_x and SO_x from flue gases operates under the conditions of pulsed corona discharges with the wire-to-plate electrode system (Fig. 2) [7]. The dimensions of each electrode, arranged in groups, are 1.5 x 2 m, and a single reactor has the productivity of 2000 Nm^3 of gas per hour. An example of high energy electron beam used for flue gas cleaning may be the installation put into service at Pomorzany power plant near Szczecin.

COMBINED PLASMA-CATALYTIC PROCESSES

Recent years have brought a considerable extension of investigation, in a new and poorly recognised area where the non-equilibrium plasma activation of molecules are coupled with the catalytic effect of solid surfaces. Although these studies still remain in their initial phase, some data obtained up till now indicate a possibility of extensive implementation of such solutions. This method can possibly increase considerably the effectiveness of catalytic installations currently applied for automobile exhaust gases cleaning. As an example of a plasma-catalytic reactor we can give an experimental, laboratory size device designed for reduction or oxidation of nitrogen monoxide (Fig. 3) [8]. The gas to be purified is passed through a barrier discharge reactor, then through a chamber filled with an appropriate catalyst (V_2O_5-WO_3/TiO_2). In another model of the reactor the decomposition nitrogen oxides proceeds in a 10 mm layer of a granular catalyst packed in the inter-electrode space, in the discharge gap (Fig. 4) [9]. Barium titanate is used as a carrier, and some metals and metal oxides have been tested as the active components. Fine-grained catalysts were also located in the discharge gap of a reactor operating under the conditions of barrier discharges, e.g. with the aim of increasing the efficiency of decomposition of some chloroorganic substances, such as CCl_4 [10]. In quite a novel design the heterogeneous catalysis has been applied for increasing the yield of nitrous oxide transformation in a gliding discharge reactor (Fig. 5) [10].

CONCLUDING REMARKS

It is first to be pointed out that coupling a plasma processes with a heterogeneous catalysis not always gives an increase of productivity of chemical processes. Among the primary conditions for obtaining favourable results (besides of using an active and selective catalyst) is the proper design of the reaction space to accommodate such a process. As it has been mentioned above, the non-equilibrium plasma provides the conditions for rapid chemical reactions with participation of short-lived, highly active species, such as excited molecules and free radicals. As generally known, a substantial role in heterogeneous catalysis is played by the transfer of reactants between the gas stream and the active surface of catalyst. The catalytic effect of such a surface may be effectively utilised only in cases where the rate of active reactants transfer from the plasma volume to the catalyst surface is sufficiently high. Otherwise the active species undergo inactivation before reaching the catalyst surface. It is therefore necessary to locate the catalyst directly in the discharge zone or very close to it, as well as to secure the efficient mass transfer between the gas and the catalyst surface. Hence, an appropriate reactor design is a fundamental condition of progress in the development of combined plasma-catalytic processes.

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PROCESY PLAZMOWE W OCHRONIE ŚRODOWISKA

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S t r e s z c z e n i e. W poszukiwaniu skutecznych metod zapobiegających degradacji środowiska zwrócono uwagę na możliwości jakie stwarzają technologie plazmowe: piroliza substancji stałych i gazowych, witryfikacja odpadów, zgazowanie substancji organicznych, oczyszczanie gazów spalinowych. Współczesne technologie plazmowe oferują wiele rozwiązań wykorzystywanych do tych celów.

S ł o w a k l u c z o w e : plazma, rozkład zanieczyszczeń, ochrona środowiska.