HETEROGENEOUS CATALYTIC SURFACE REACTIONS IN NON-EQUILIBRIUM PLASMAS

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I. INTRODUCTION

Heterogeneous catalytic phenomena are possible in plasma synthesis. Experimental studies realised include synthesis of NO (1,2), of NH_3 (3), of HCN (4), of anhiline (5), of hydrazine (6), decomposition of NH_3 (7) of hydrocarbons (8). Other particular cases of heterogeneous catalysis in electrical discharges concern surface treatment of polymeric films (9) and ozone production (10).

Low pressure plasmas are non-equilibrium systems. Gas-phase reactivity in such systems is different from equilibrated "thermal" systems (11). Some theoretical and/or experimental studies have been realized in simple non-equilibrium media, like molecular beams. An extension of the conclusions of these studies to the gas phase plasma reactions has already be attempted (12).

In this paper we study for the first time the correlation between the non-equilibrium excitation of the plasma and the efficiency of the catalytic surface reactions. It appears that the high vibrational and electronic excitation favours the surface reaction.

We establish also the existance of two new phenomena : the formation of a boundary film near the catalytic surface and an exceptional energy transfer to the solid. An interpretation of these phenomena is proposed. Finally we underline the importance of catalytic process for the energy yield of the reactor.

II. GAS PHASE CHEMICAL REACTIVITY

The systematic study of the reactivity of a non-equilibrium medium has be realized by Polanyi (11) in the absence of electronic excitation. Also, in his experiences, only one degree of freedom were excited at once. The main conclusion is that endothermic reactions are favoured by preferential vibrational excitation of the reactants, when exothermic processes are favoured by high translational excitation.

Because of the complexity of non-equilibrium plasmas, the application of these conclusions should be carefull. For example, in two endothermic reactions like NH_3 decomposition (NH_3 plasma) and HCN synthesis (in a $N_2 + CH_4$ plasma) the former reaction is favoured by a high vibrational temperature and the later by a high translational temperature (fig. 3,4).

Our conclusion is that in a plasma chemical reactor one must not consider the global reaction, but analyse it in three successive steps (excitation, "hot" reactor, quench). Each step constitutes a separete "reaction" with a reactant and a rather long life-time product. Polanyi's rules should be applied to these individual reaction steps. For example for NH_3 decomposition the global reaction is controlled by the endothermic step of NH_2-H bond dissociation (excitation) and thus is favoured by high vibrational temperature. In the case of HCN the global synthesis is controlled by the exothermic step of evacuation of excess energy from the product molecule and thus it is favoured by a high transla-

tional temperature.

III. EXPERIMENTAL STUDY OF HETEROGENEOUS CATALYSIS

In order to study the relation between the heterogeneous catalytic efficiency and the non-equilibrium nature of low pressure plasmas, we used the plasma reactor already described (12) : a low pressure (1 to 40 mbar) plasma is created by inductively coupled HF discharge in a 0,10 m large and 0,20 m long pyrex tube. At the end of the reaction the plasma is quenched in a water-cooled Cu surface. Spectroscopic analysis of plasma's emission is also performed. A grid of the metal used as catalyst (Mo or W) is placed in the plasma torch, near the quench.

The reactions studied is nitrogen fixation as HCN (in a N_2 + CH_4 plasma) et NH_3 dissociation.

An important catalytic effect was observed (fig. 1,2). Nitrogen fixation rate and NH_3 decomposition rate increase by a factor of 50 % or more. Mo is a more efficient catalyst for N_2 fixation, but W is more efficient in the case of NH_3 decomposition.

Like in the gas phase reaction, the efficiency of the heterogeneous reaction varies with the non-equilibrium degree of the plasma α (fig. 3, 4) : in both cases the catalytic effect increases with increasing non-equilibrium degree. This indicates that the controlling step of the catalytic process is the same in both cases (unlike the gas phase reactions).

IV. THEORY OF HETEROGENEOUS CATALYSIS IN A NON-EQUILIBRIUM PLASMA

The heterogeneous catalytic process involves three successive steps : adsorption of the reactants on the surface of the catalyst ; reaction of the adsorbed species on the surface ; desorption of the products.

The only theretical treatment of heterogeneous catalysis in the case of non-equilibrium gas phase system has been carried out by Wolken and coworkers (13). They used for their calculations simple reacting systems (H_2 dissociation, O_2 adsorption) and they did not consider electronic excitation of the gas. This calculations have not yet be experimentally confirmed.

Like in the case of Polanyi's studies of gas phase reactivity, the extention of Walken's conclusions to low pressure plasmas should not be a simple transposition. An adaptation is necessary, because of the presence of excited electronic states and the multiform excitation of molecules in the plasma.

a. Influence of non-equilibrium on adsorption

There are three types of adsorption : activated adsorption (with on energy barrier), adsorption without energy barrier and spontaneous adsorption (attractive energy potential).

Wolken's calculations show that in the first two cases preferential vibrational excitation of the reactants will favour the adsorption process.

Experience in plasma confirms this conclusion : as shown in fig. 3 and 4 the efficiency of the catalytic process is enhanced when the non-equilibrium degree α, i.e. vibrational excitation, is increased.

The electronic excitation of the molecules in the plasma is higher when non-

equilibrium is increased. These states chemisorb very easy, because of their different orbital (space) symmetry. So, catalytic reactions from electronic excitation in also favoured by non-equilibrium.

b. Influence of non-equilibrium on surface reaction

The influence of vibrational excitation of the gazeous phase on the surface reaction is not well established. It seems however that the high vibrational excitation of the gas is transferred to the solid-adsorbate bond, facilitating the diffusion on the surface (i.e. the reaction probability) and the desorption of the products. The favourable effect on the catalytic reaction is however limited by the possibility of activating at the same time the desorption of the adsorbed reactants.

c. Non-equilibrium excitation of the reaction products

At the end of the heterogeneous reaction the energy balance between the bond energy of the products and their desorption energy is often in excess. The desorbed gaseous molecule conserves a great part of this excess energy, and some times all of it (14). The theoritical calculations of Wolken indicate that this excess will be chanelled to the vibration of the molecule in the case of quasi-symmetric molecules. For highly asymmetric molecules, the vibrational and translational excitation of the desorbing molecules will be equal.

Our experiences confirm theritical conclusion. For example, in the case of NH_3 catalytic decomposition

$$NH_3 \xrightarrow[\text{or W}]{\text{Mo}} N_2 + H_2$$

the spectroscopic analysis of the gas in the close vicinity of the catalyst surface shows the existance of a boundary film in which the vibrational excitation of N_2 is significally higher that in the bulk of the plasma (fig. 5). Similar results were obtained for the catalytic dissociation of N_2.

In this boundary a V-V transfer is taking place from the desorbing N_2 to the adsorbing NH_3. This "feddback" transfer will increase the efficiency of NH_3 dissociative adsorption, and so the catalytic effect.

This particular excitation of the boundary film depends on the nature of catalyst and disappears when the catalytic metal (Mo or W) is replaced by a non-catalytic one (Zn) (fig. 5).

V. ENERGY TRANSFER TO THE SOLID DURING THE CATALYTIC PROCESS

When the surface reaction-desorption sequence is exothermic, a variable part of the excess energy is transferred to the solid. The sharing of excess energy (accomodation coefficient) between the desorbing product molecule and the catalyst depends on the nature of the catalyst and of the gas, the reaction mecanism (Langmuir-Hinshelwood or Rideal), the translational temperature of the reactor (14).

If the catalytic process takes place in a low-pressure reactor, the temperature of the solid catalyst will be different from the gas (translational) temperature. A well known example is the experience of lord Raleygh in 1940's, when he observed an "abnormal" overheating of catalytic metals (Pt, Pd) in a glow discharge of nitrogen (15).

This overheating of the catalyst (which sometimes melts in the "cold" plasma) is

the result of two processes : first, partial transfer of excess energy of the reaction-desorption sequence to the solid. The energy involved may be important (about 5 eV in the N_2-W system) and the rate of this transfer is significant in the Langmuir-Hinshelwood type reactions.

Second, transfer of the high vibrational excitation of the plasma to the solid. Transfer of this type is rather inneficient, except when physisorbed species acte as intermediaries in the catalytic systems. We can suppose that this transfer is efficient in the heterogeneous catalytic systems, if presursor states of adsorption and desorption act as intermediary.

VI. ENERGY YIELD OF THE PLASMA REACTOR

Energy yield of plasma reactors is generally low. Indeed, as excitation in the discharge is not selective, an important part of the induced energy is consummed by the excitation of non reacting low energy states. For example, in the case of N_2 plasmas, most of energy is consummed for the population of the metastable $N_2A^3\Sigma u$ state or by the vibrational excitation of the ground state $N_2X'\Sigma g^+$, which do not fixe nitrogen by gas-phase reaction.

Preferential excitation of high energy electronic states will increase the chemical yield of the reactor but not its energy yield. For instance, if we synthezise NO by preferential excitation of the very reactive N_2^+ ion, energy yield of the reactor will be 13 % at best (i.e. by supposing 100 % chemical yield). If we use for this synthesis the dissociative $N_2C^3\Pi u$ state the energy yield will not exceed 20 % (fig. 6).

The catalytic processes described in this paper are the only realistic solution of the problem of reactor yield. For example if the NO synthesis is realized via the excited $N_2A^3\Pi u$ state (or the fundamental vibrationally excited) the energy yield will reach 31 %.

CONCLUSION

Chemical reactivity of non-equilibrium media depends not only on the quantity of available energy but also on the disposal of this energy on the different excitation modes of the molecules.

We proposed the extention to low pressure plasmas of the rules on chemical reactivity established in more simple systems. Our conclusion is that this extension is possible under two conditions : first, to consider also the specific reactivity of electronically excited molecules, and second to separate the global reaction in three successive steps : excitation, "hot" reactor, quench.

Heterogeneous catalysis in non-equilibrium plasmas differs from classical thermal systems in many points of view :
First the exceptional vibrational and electronic excitation in the plasmas promotes chemisorption.
Second, in the immediate vicinity of the catalyst surface a gas film is formed in which internal excitation of the molecules is significally higher then in the rest of the plasma. This phenomenon is owe to the high vibrational excitation of the desorbing product molecules at the end of the catalytic sequence. The V-V transfer from products to reactants in this film promotes by a "feedback" mecanism the efficience of the chemisorption.
Third, the catalyst is overheated (and sometimes melt) in the reactor. Two process contribute to this phenomenon : transfer of the vibrational excess energy of the reaction-desorption sequence. This late process constitutes a very

efficient quench for the products.
Finally, when the atoms of the solid participates to the synthesis reaction by a cyclic mecanisme (example : WO_3) the high excitation of the plasma accelerates the "reconstruction" of the catalyst, i.e. the reaction cycle.

1 - AMOUROUX J., CAVADIAS S., RAPAKOULIAS D., Rev. Phys. Appl., 1979, 14, 269.
2 - BARDONNET J.M., Thèse, Université de Limoges, 1978.
3 - BOTCHWAY G., VENUGOPALAN U., Z. Phys. Chemie, 1980, 120(1), 103.
4 - RAPAKOULIAS D., AMOUROUX J., J. Rev. Phys. Appl., 1979, 14, 961.
5 - BROOKS B.W., SEAPORT R.M., J. App. Chem. Biotech., 1974, 24, 621.
6 - EREMIN E.N., RUBATSOVA V., Russ. J. Phys. Chem., 1973, 47(1), 356.
7 - RAPAKOULIAS D., AMOUROUX J., Rev. Phys. Appl. to be published.
8 - MOEBUS P., J. Electroch. Soc., 1975, 122(2), 298.
9 - AMOUROUX J., GOLDMAN M., REVOIL M.F., this symposium.
10 - LECUILLER M., Thèse, Université Paris-Sud, 1980.
11 - POLANYI J.C., Acc. Chem. Res., 1972, 5, 161.
12 - RAPAKOULIAS D., AMOUROUX J., in 4th International symposium on plasma chemistry, University of Zürich, (editor S. Veprek), Zürich 1979, p. 372.
13 - PURVIS G.D., REDMON M.J., WOLKEN G.J., J. Phys. Chem., 1979, 83(8), 1027.
14 - HALPERN B., ROSNER D., J. Chem. Soc., Farad. Trans., 1978, 8, 1883.
15 - RAYLEIGH, Proc. Roy. Soc., 1940, 176(1), 16.

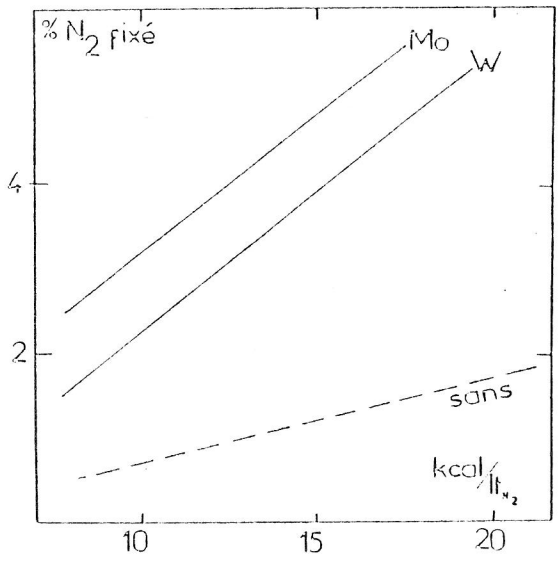

Fig. 1 : Catalytic effect in the synthesis of HCN

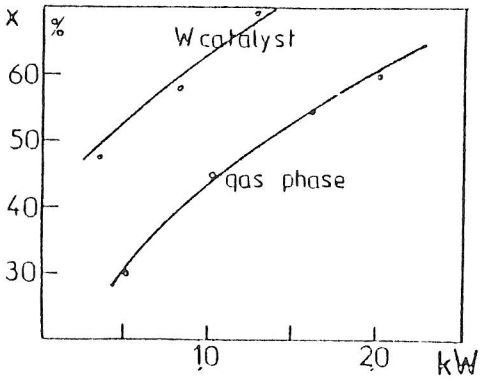

Fig. 2 : Catalytic effect in the decomposition of NH_3

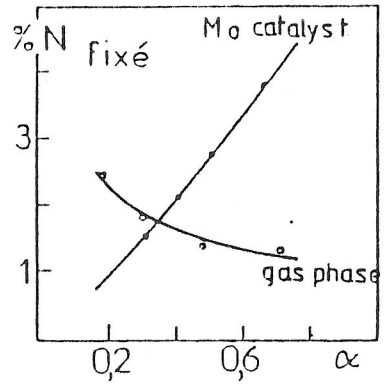

Fig. 3 : Variation of the rate of HCN synthesis as a function of non-equilibrium degree of the plasma α

$$\alpha = \frac{T_{vib} - T_{transl}}{T_{vib} + T_{transl}}$$

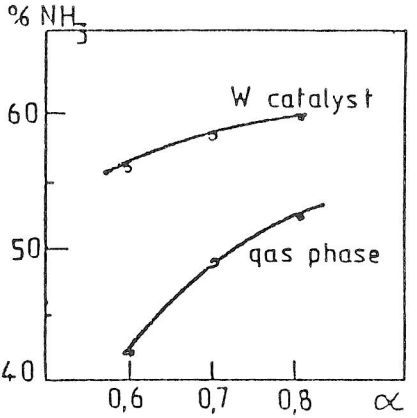

Fig. 4 : Variation of the decomposition rate of NH_3 as a function of non-equilibrium degree of the plasma

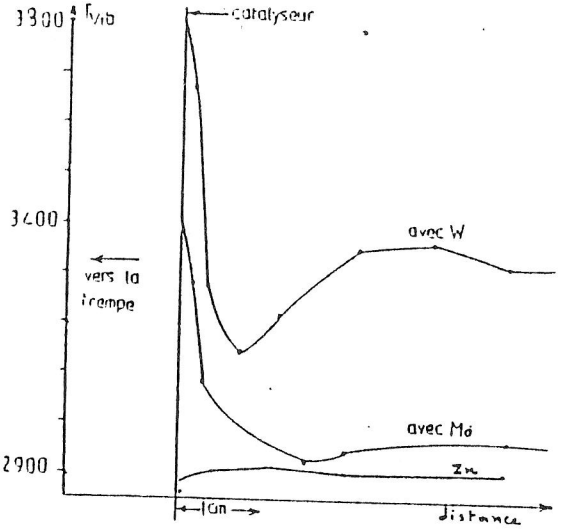

Fig. 5 : Increase of vibrational excitation near the catalyst surface ("boundary film")

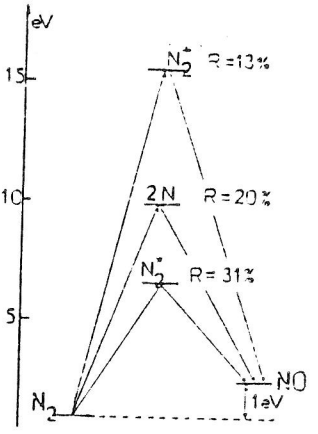

Fig. 6 : Theoretical energy yield for the NO synthesis as a function of three possible ways