SENSITIZED CONVERSION OF METHANE TO ACETYLENE AND ETHYLENE BY ADDITIONS OF HG-VAPOUR IN A THERMAL PLASMA

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Keywords: Sensitizing, plasma reactions

Compounds: Methane conversion to acetylene/ethylene

ABSTRACT

The conversion of methane to acetylene/ethylene in a thermal plasma was sensitized by means of Hg-vapour additions. The Hg-additions cause an increase of acetylene and ethylene yields up to 24 and 250%, resp. The effect was explained by an additional decomposition of CH_4-molecules due to energy transfer processes from metastable excited Hg-atoms.

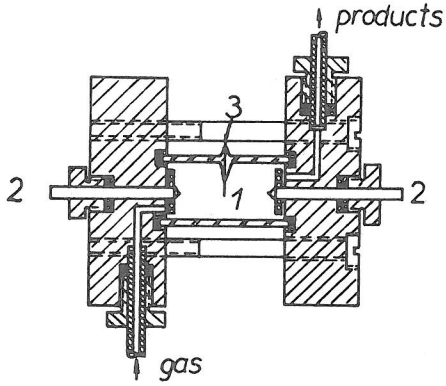
1. INTRODUCTION

Sensitizing effects are well known in plasma chemistry. They can cause a remarkable increase in rate constants which lead to an increase in the yields of reaction products and to a reduction of specific energy amount for its synthesis. Sensitizing effects may be achieved as well by means of gaseous additions to the plasma system as by enlargement of the boundary surfaces of the plasma; they are called sometimes as plasma catalysis and are mainly observed under nonthermal conditions. Examples of plasma catalysis are the increase of methane cracking to acetylene and the improvement of ammonia synthesis from N_2 and H_2 in a glow discharge due to additions of Hg-vapours and He-atoms, resp. / 1 /. In the case of heterogeneous plasma catalysis

due to the presence of a Pt-grid in the discharge tube the NH_3-yield from N_2 and H_2 could be increased by a factor > 10 / 2 /. Sensitizing effects can also be achieved under thermal plasma conditions. The methane cracking in an electric arc was sensitized by a 3 - 4% addition of a propane/ butane mixture which lead to an increase of the conversion degree for C_2H_2 from 42 to 62% and to an enhancement of acetylene concentration in the pyrolysis gas from 9,5 to 13% / 3 /. An sensitizing effect was also observed in a plasma jet after adding W- and Al-powders, resp. The metallic additions cause an increase of the conversion degree of propane to acetylen from 67 to 93% / 4 /. These effects can be explained by energy transfer processes from metastable excited atoms or molecules of the sensitizing "catalysator" and by a dissociative charge transfer causing an additional formation of ionic and radicalic reaction species. The sensitization can also be interpreted by a 3 body impact mechanism in which the sensitizing species stabilize the product molecules by taking off the reaction energy.

2. EXPERIMENTAL and RESULTS

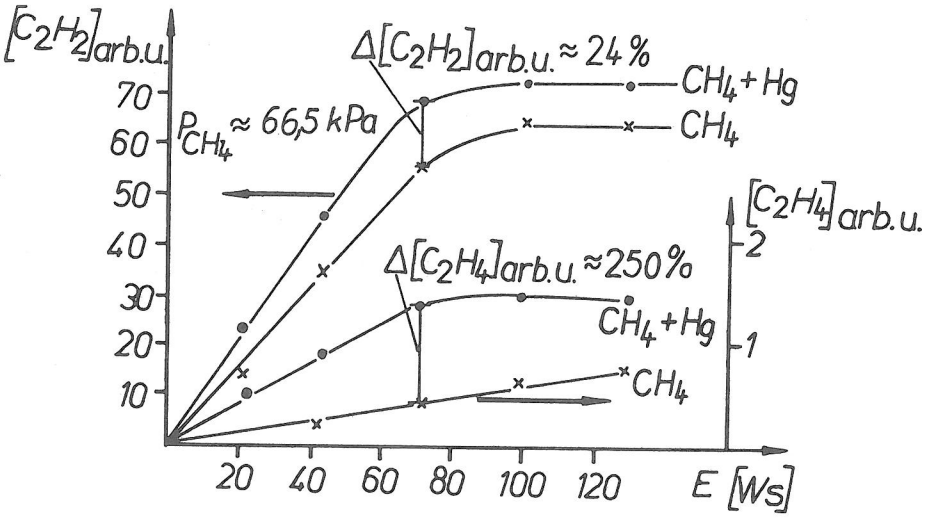
The present investigations concern the sensitizing of methane pyrolysis to acetylene/ethylene in a thermal plasma. The sensitizing effect should be realized by several metalvapours. The investigations were performed under model conditions in a nonstationary arc plasma. The use of a sparc-arc is recommendable because of the extraordinary simplicity of the reactor and the free choise of the reaction system and the operation parameters. The sparc discharge makes it possible to study the sensitizing effect under high-energetic conditions with energy inputs of several MW. The scheme of the reactor is presented in fig. 1. The main part of the reactor is the sparc chamber (1) consisting of a cylindrical quartz tube (Ø 20 mm) with isolating plates at its ends. The plates served as holders for the electrodes (2). The chamber had a volume of 8 cm^3. The electrode di-



stance could be varied between 3 - 16 mm. The sparc was triggered by an ignition device (s. trigger electrode (3)). The initial voltage of the sparc-arc had values of some kV and the discharge current rose up to several 10^4 A during a discharge time of 10^{-5} sec, which lead to power values of 8 - 10 MW. The power input was determined oscillographically. The measurements took place under static conditions. The reaction products were analysed by means of a gas chromatograph. The metallic vapours with which the methane pyrolysis should be sensitized were introduced into the sparc chamber via the electrodes (2). For this purpose the electrodes were performed as thin wires (Ø 1mm), which vapourize during the discharge. The product yields of acetylene and ethylene were measured in dependence on methane pressure in the chamber at a constant energy input. The results of the measurements are presented in the following table. The values in the table indicate that with exception of amalgamated Cu no other of the investigated metal vapours causes a considerable sensitizing effect on methane pyrolysis. In the case of amalgamated Cu Hg-vapours should be responsible for the observed effect. The yield increase at higher pressures refers to the importance of secundary impacts at the sensitizing processes.

Electrode material	p_{CH_4} : 50 Torr (6,7 kpa)		p_{CH_4}: 500 Torr(67 kPa)	
	$h_{C_2H_2}$ [mm]	Δh against a Fe-electrode	$h_{C_2H_2}$ [mm]	Δh against a Fe-electrode
Fe	221	-	169	-
Al	216	-2,2 %	168	± 0 %
Cu	214	- 3 %	161	-4,7 %
W	217	-1,8 %	180	+6,5 %
Sn	223	+ 1 %	175	+3,3 %
Hg (amalgam. Cu)	234	+ 6 %	206	+ 22 %

To reveal the sensitizing effect observed with Hg-vapour further investigations were performed with a Hg-electrode instead of the wire electrode. The Hg-electrode consisted of a ceramic container filled with liquid Hg. With regard to alter the vapourization amount of Hg into the pyrolytic system the acetylene and ethylene yields, resp. were measured by varying the energy input to the reactor. The yields in the presence of Hg were compared with analogous yields from measurements using a ceramic covered Fe wire instead of the Hg-electrode. The Hg-electrode was switched as cathode. The conversions took place at a methane pressure of 500 Torr (= $67 \cdot 10^3$ Pa), a voltage of 3 kV and a sparc length of 16 mm. The results of the measurements are presented in fig. 2. The curves show the yields of acetylene and ethylene in dependence of energy input to the sparc in the presence and absence, resp. of Hg-vapours in the plasma system. The curves indicate that the presence of Hg-vapour in the plasma leads to an increase of acetylene as well as of ethylene yields in the whole range of energy input. The highest sensitizing effect corresponds to an yield improvement of 24% for acetylene and of 250% (!!) for ethylene. As a consequence of these results remarkable



reduction of the specific energy amount for acetylene synthesis from methane by means of Hg-vapour additions can be concluded.

3. DISCUSSION

To explain the observed effects it is obvious to assume that the thermal equilibrium of the pyrolytic C/H-system is superimposed by activating metastable excited Hg-atoms. Its high energetic triplett states - the 6^3P_1-levels at 4,88 eV, the 6^3P_2-levels at 5,44 eV and the $^3D_1$-level at 9,06 eV - make Hg-atoms most favourable for sensitizing processes. The energy of these states is sufficient to detach H-atoms from methane molecules and from its dissociation products, resp. accordingly to the processes

$$CH_n + Hg^* \longrightarrow CH_{n-1} + H + Hg \quad (n = 4,3,2)$$

In the presence of Hg-atoms in the pyrolytic system more C/H-radicals with fewer H-atoms were built than under conditions of pure thermal equilibrium. A similar mechanism was postulated for explaining the sensitizing effect of Hg-atoms

under photochemical conditions / 5 /. The C/H-radicals recombine during the quenching process, and the higher content of H poor radicals causes higher yields of athylene and acetylene molecules, resp. This mechanism is additionally revealed from dwell time investigations on a shock tube which lead to the conclusion that the acetylene yield strongly depends on the recombination of CH-radicals. This effects necessarily a decrease of the activation energy for the formation of acetylene and as a consequence an increase of the rate constant, the typical effect of plasma catalysis.
The sensitizing effect by means of Hg-vapours was also observered on other alkanes. Because of the strong analogy between the chemical conversions in a stationary and a non-stationary thermal plasma we are convinced that the present sensitizing effect will be realized in every kind of thermal plasmas.

4. REFERENCES

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