

REACTION OF METHANOL IN ELECTRIC DISCHARGE GENERATED AT THE FERROELECTRIC SURFACE¹⁾

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The reaction of methanol vapours in electric discharge generated at the ferroelectric surface was investigated. The parameters determining the chemical reaction effect were found to be the energy supplied to the system and the residence time of the reagents in the discharge zone (pressure 1027 hPa, flowing conditions). Probable reaction channels were described.

РЕАКЦИИ МЕТАНОЛА В ЭЛЕКТРИЧЕСКОМ РАЗРЯДЕ, ГЕНЕРИРОВАННОМ ПРИ ПОВЕРХНОСТИ СЕГНЕТОЭЛЕКТРИКА

В работе приведены результаты исследований реакций паров метанола в электрическом разряде, генерированном при поверхности сегнетоэлектрика. Обнаружено, что параметрами, которые определяют эффективность данного химического процесса, являются энергия, подводимая в систему, и время пребывания реагентов в зоне разряда (давление 1027 гПа, характеристики потока). Обсуждены также возможные каналы реакции.

1. INTRODUCTION

A general description of the chemical reactions taking place under non-equilibrium conditions of electric discharge plasma is difficult owing to the multichannel character of the process.

Thus, attempts to find generalized macroparameters result from these considerations, which determine the direction of the chemical reaction in a given type of discharge and in the further stage, their connection with microparameters, which characterize the course of reaction in non-equilibrium plasma of the electric discharge [1, 2].

One of the characteristic parameters postulated is the specific energy, determined by the ratio of power supplied to the system and volume intensity of the

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substrate flow. The reciprocal of the volume intensity flow is regarded as being proportional to the reaction time [2].

The electric discharge employed is an effect of interaction of an alternating electric field on the ferroelectrics sample. This field causes some changes in the domain structure of the sample and appearance of strong local electric fields at its surface. A thin gaseous plasma layer was generated at the ferroelectrics surface [3]. The discharge takes place in the interelectrode area and the area volume depends on the size, distance, and shape of the electrodes. Thus, the residence time of the substrate in the discharge area (τ) can be evaluated from the basic equation

$$V\phi_0 = 2\pi r a v(r)\phi. \quad (1)$$

It was assumed that $\phi_0 = \phi$ owing to small amounts of the reaction products as compared with those of gases flowing through the discharge area. The gas temperature is constant and the pressure drop is practically equal to zero ($\Delta p = 2 \text{ mm Hg}$ in comparison with 770 mm Hg). Thus, after transformation of (1)

$$\tau = \frac{\pi a}{V} (r^2 - r_1^2) \quad (2)$$

was obtained.

II. EXPERIMENTAL ARRANGEMENT

The reactor diagram and procedure of substrate addition to the discharge zone are given in Fig. 1. The discharge was generated by high voltage a. c. of the

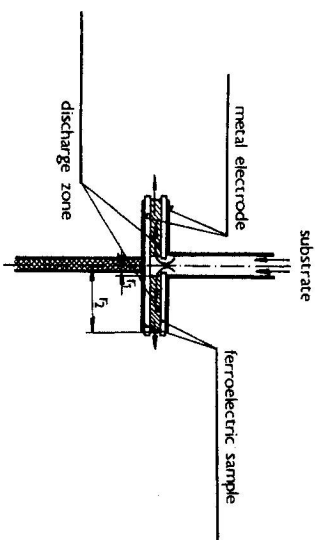


Fig. 1. Diagram of the reactor and procedure substrate supplying the discharge zone.

frequency 50 Hz between two circular ferroelectric plates of the same (and not changeable) thickness. In all the experiments the distance between ferroelectrics plates (ceramics, main component barium titanate, relative electric permittivity 6000, Curie temperature 309 K) was constant.

The experiments were performed under the pressure of 1027 hPa (770 mm Hg) in following conditions. Methanol vapours were introduced into the discharge zone by carrier gas (argon). The reaction was carried out in a reactor thermostated at the temperature of 343 K to avoid condensation of methanol vapours. The receiver of unreacted methanol (a vessel placed in a cooling mixture equipped additionally with a freezing finger) was placed behind the reactor.

The content of methanol flowing through the discharge zone in a time unit was determined from the mass loss in the evaporator and evaporation time. The volume intensity of the argon flow was measured with a flow meter.

The gaseous products were analysed by gas chromatography.

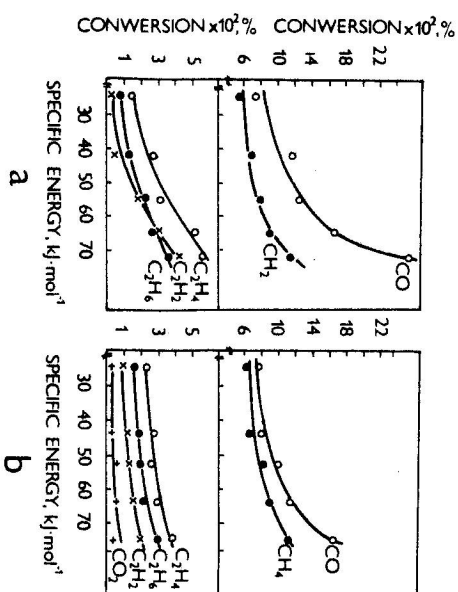


Fig. 2. Relation between the conversion degree of methanol to CO, CH₄, C₂H₄, C₂H₂, and CO₂ and the specific energy of methanol for the residence time of gases in the discharge zone equal to: a) $1.1 \times 10^{-2} \text{ s}$; b) $2.6 \times 10^{-2} \text{ s}$.

III. RESULTS

Three series of experiments were performed. In the first constant values of molar flow of methanol and argon were kept ($V_m = (1.48 \pm 0.18) \times 10^{-4} \text{ mole s}^{-1}$; $V_a = (1.53 \pm 0.06) \times 10^{-4} \text{ mole s}^{-1}$). The power supplied to the system was chargeable and so was the specific energy. The residence time of gases in the discharge area was constant and equal to $(1.1 \pm 0.1) \times 10^{-2} \text{ s}$.

The second series of experiments was carried out similarly. The residence time in the discharge zone was longer and amounts to $(2.6 \pm 0.2) \times 10^{-2} \text{ s}$, attained by changing the molar flow of methanol and argon: $V_m = (1.08 \pm 0.11) \times 10^{-4} \text{ mole s}^{-1}$; $V_a = (2.0 \pm 0.1) \times 10^{-5} \text{ mole s}^{-1}$.

The results of experiments are given in Fig. 2. In the third series of experiments (Fig. 3), a constant specific energy of methanol $54.5 \pm 1.4 \text{ kJ mole}^{-1}$ was maintained over the whole series by selecting proper values of molar gas flow and discharge powers. The residence time of gases in the discharge area was changed from $1.0 \times 10^{-2} \text{ s}$ to $3.4 \times 10^{-2} \text{ s}$.

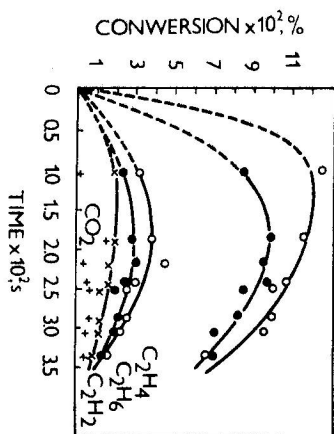


Fig. 3. Relation between the conversion degree of methanol to CO, CH₄, C₂H₆, C₂H₄, and CO₂ and the residence time of gases in the discharge zone for the specific energy of methanol $54.5 \text{ kJ mole}^{-1}$.

IV. DISCUSSION AND CONCLUSIONS

The two first series of experiments (Fig. 2a, b) indicated that, under the process conditions, the residence time of the reagents in the glowing zone and the energy supplied to the system were determined by the reaction course, since the specific energy was in this case a formal parameter only.

In the discharge type used, the residence time depends not only on the reciprocal of the substrate flow intensity but also on the geometry of the system (formula 2), which limits the use of specific energy as a normalizing parameter. In the system of a constant construction a change of the residence time at constant specific energy decidedly changed the effect of the process, the more so as the changes of powers and molar intensities of the methanol flow did not exceed 25 % of the mean value. The time was adjusted by changing the argon flow intensity. The specific energy can therefore be a parameter useful only for the comparison of results of various powers and volume intensities of the substrate flow but the same residence times.

In the experiments powers were employed which did not exceed 10–20 watts and glowing zone volumes ($< 0.1 \text{ cm}^3$) small in comparison with the volume of the gas flowing in a time unit ($2.9 \text{ cm}^3 \text{ s}^{-1} \div 8.9 \text{ cm}^3 \text{ s}^{-1}$). Low conversion degrees of methanol were, therefore, obtained.

The main gaseous reaction products were: H₂, CO and CH₄ and by-products (concentrations lower by one order of magnitude) C₂H₄, C₂H₆, C₂H₂. An increase of the discharge power at a short residence time (Fig. 2) raised the methanol-to-CO

conversion degree in comparison with that for CH₄. The conversion degree to C₂H₄ is higher than that to C₂H₆. CO₂ was detected for longer residence time only.

It can be assumed, therefore, that CH₄ (precisely $\dot{\text{C}}\text{H}_3$) is an intermediate in the reaction of the CO formation. This is confirmed by the results of methanol vapours decomposition in a high frequency discharge (10 MHz, 20 mm Hg, 1125 W). For much higher powers the main products are H₂ and CO ($> 20 \text{ vol. \%}$). There was CH₄ less than C₂H₂ ($< 2 \%$) [4].

The excited methanol molecule is a source of $\dot{\text{C}}\text{H}_3$ and $\dot{\text{O}}\text{H}$ radicals. Recombination of $\dot{\text{O}}\text{H}$ radicals in the presence of argon is a very fast process being a source of O atoms, which oxidized methyl radicals (very fast reaction [5]).

List of the symbols used

ρ_0 — density of gases prior to introduction into the discharge zone, ρ — density of gases passes in the discharge zone, r — ferroelectric sample radius, a — distance between the samples, V — volume intensity of gas flow (total volume intensity of argon and methanol vapours flow under experimental conditions), $v(r)$ — gas stream velocity along the ferroelectric sample radius.

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