The presented results of methane oxidative coupling indicate that the lowering of the reaction temperature below 700°C, without any loss of its effectiveness, requires a much longer contact time than the times applied in a great majority of studies reported so far.

**Keywords:** methane conversion; methane oxidative dimerization; methane oxidative coupling; Li⁺–MgO catalyst; Li⁺–(MgO + Dy₂O₃)–Cl⁻ catalyst; reaction conditions (temperature, contact time); activity; selectivity (C₂⁺ hydrocarbons)

### 1. Introduction

The lowering of the temperature of every high-temperature process, while entailing no yield loss, always constitutes a challenging and desirable aim of research. This is also the case of methane oxidative coupling. So far there have been few reports [1–7] about catalysts on which good yields of higher hydrocarbons (C₂⁺) were obtained at temperatures of about 600–650°C, that is, by 100–200°C lower than in the case of all the other known catalysts. Some of these reports have not been confirmed in further studies; for instance, attempts to reproduce the results obtained over Na⁺ doped zirconia (refs. [8–10] versus ref. [2]) and calcium–nickel–potassium oxide (refs. [11,12] versus refs. [3,4,7]) catalysts, ended to failure. From among other studies the most interesting results have been reported by Lunsford [6]. Employing Li⁺–(MgO + Dy₂O₃)–Cl⁻ catalyst at the temperature of 600°C he obtained a 26.5% conversion of methane with the C₂⁺ hydrocarbon selectivity and yield of 50% and 12.8%, respectively.

In this work it has been established that the effective reaction at moderate temperatures results not only from the quality of the catalyst but also, and first of all, from the conditions of the reaction, at least for some catalysts. Of special significance is the contact time of the reaction mixture with the catalyst.
2. Experimental

The catalyst Li$^+$–MgO (4 wt% of Li$^+$) was prepared by magnesium oxide impregnation with an aqueous solution of lithium nitrate and calcination at 750°C for 16 h. The catalyst Li$^+$–(MgO + Dy$_2$O$_3$)–Cl$^-$ was prepared according to the description given by Lunsford [6].

The reaction of methane oxidative coupling was carried out at the atmospheric pressure in a quartz reactor with an internal diameter of about 10 mm, narrowing down to about 3 mm behind the catalyst layer; this shape increased the rate of post-reaction gas removal from the reaction zone and restricted the possibility of secondary transformations of reaction products beyond the catalyst. The reactor contained 0.5 or 1.5 g of the catalyst. Reaction temperature was measured in the catalyst layer.

The reaction mixture, consisting of methane, oxygen and nitrogen ($p$(CH$_4$ + O$_2$) = 0.39 atm and CH$_4$ : O$_2$ = 2.7 : 1 (as in ref. [6]) or $p$(CH$_4$ + O$_2$) = 0.59 atm and CH$_4$ : O$_2$ = 4.8 : 1) was fed to the reactor at a rate which ensured the attainment of modified contact times $W$/$F$ ($W$ – catalyst mass; $F$ – flow rate of the reaction mixture), equal to 0.6 or 10.0 s g/cm$^3$.

The results presented in the paper concern stationary properties of the catalyst, when no CO$_2$ was captured by the catalyst or released from it. The analysis of the reaction was performed by on-line gas chromatography on Porapak Q and molecular sieves 4A + 5A. The selectivity and degree of methane conversion were calculated with a correction introduced for the change in gas volume during the reaction.

3. Results and discussion

The results obtained during methane oxidative coupling are presented in figs. 1–4.

The total methane conversion (fig. 1) depends significantly on the $W$/$F$ contact time and on the composition of the reaction mixture. For a short contact time a considerable improvement occurs only above 650°C – such temperature dependence is similar to that of the majority of the known catalysts. An effective lowering of reaction temperature becomes possible only after a significant lengthening of the contact time. At temperatures below 700°C the increase in methane conversion with an extended contact time was higher for Li$^+$–(MgO + Dy$_2$O$_3$)–Cl$^-$. The composition of the reaction mixture had different effects on reaction course over both catalysts at temperatures below and above 700°C. Over Li$^+$–MgO at low temperatures, in spite of a larger amount of oxygen in relation to methane, the lower partial pressure of the reagents yields a lower methane conversion. A reverse situation occurs at high temperatures and in the whole temperature range on Li$^+$–(MgO + Dy$_2$O$_3$)–Cl$^-$. Under the reaction conditions as described in ref. [6] the