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Oxidative coupling of methane at moderate (600–650°C) temperatures

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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^+–($MgO+Dy_2O_3$)–Cl^- catalyst; reaction conditions (temperature, contact time); activity; selectivity (C_{2+} 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 (C_{2+}) 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^+–($MgO + Dy_2O_3$)–Cl^- catalyst at the temperature of 600°C he obtained a 26.5% conversion of methane with the C_{2+} 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.

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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^+–$(MgO + Dy_2O_3)$–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^+–$(MgO + Dy_2O_3)$–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^+–$(MgO + Dy_2O_3)$–Cl^-. Under the reaction conditions as described in ref. [6] the

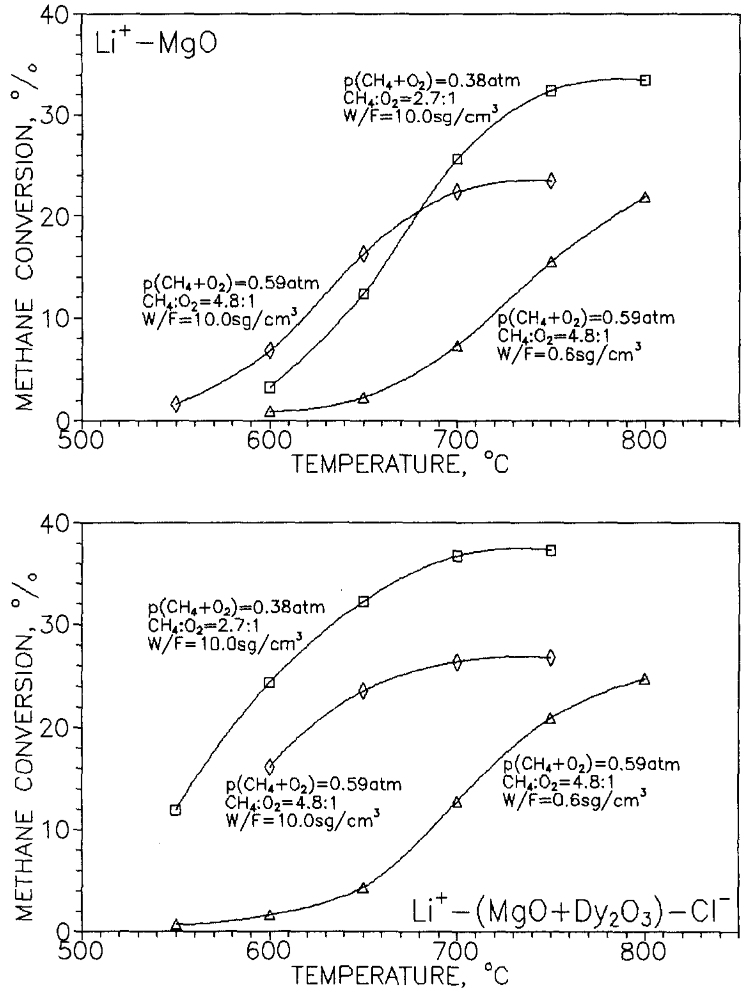

Fig. 1. Effect of reaction conditions on methane conversion.

results obtained on the latter catalyst were quite similar to those quoted previously.

A longer contact time ensures an increase by several scores of per cents in the selectivity of C_{2+} hydrocarbon formation at the temperature of 600°C (fig. 2) to values similar for both catalysts. With a short contact time, the selectivity of C_{2+} formation over Li^+–($MgO + Dy_2O_3$)–Cl^- at that temperature is considerably smaller than over Li^+–MgO. Hence, with extended contact time, the increase in selectivity is larger. The longer contact time becomes detrimental only at temperatures higher than 650°C.

The yield of C_{2+} hydrocarbons, as a consequence of total methane conversion and selectivity, depends first of all on the *W*/*F* contact time (fig. 3). Similarly to rises in methane conversion and selectivity, the increase in the yield at 600°C, after

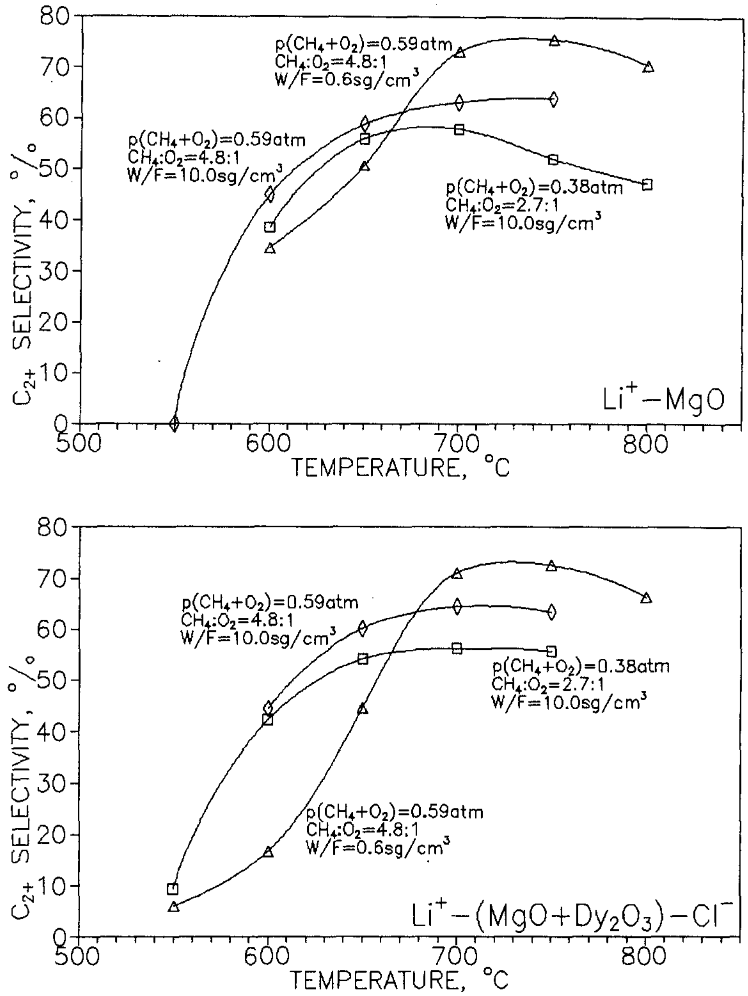

Fig. 2. Effect of reaction conditions on C_{2+} hydrocarbon selectivity.

contact time extension, is larger in the case of Li^+–(MgO + Dy_2O_3)–Cl^- than in that of Li^+–MgO. The lowering of the reaction temperature, with the yield unchanged, possible after contact time extension, is also larger for catalyst Li^+–(MgO + Dy_2O_3)–Cl^-. A maximum yield of about 16%, obtained with a short contact time at 800°C, can be achieved with a higher W/F, without changing any other reaction conditions (and, obviously, of the catalyst itself), already at a temperature lower by about 100°C for Li^+–MgO and 150°C for Li^+–(MgO + Dy_2O_3)–Cl^-. The composition of the reaction mixture affects the yield of hydrocarbons in the similar way as total methane conversion.

At the same time, the effect of the W/F contact time on the temperature dependence of the degree of oxygen (fig. 4) is evident. This second reagent is responsible

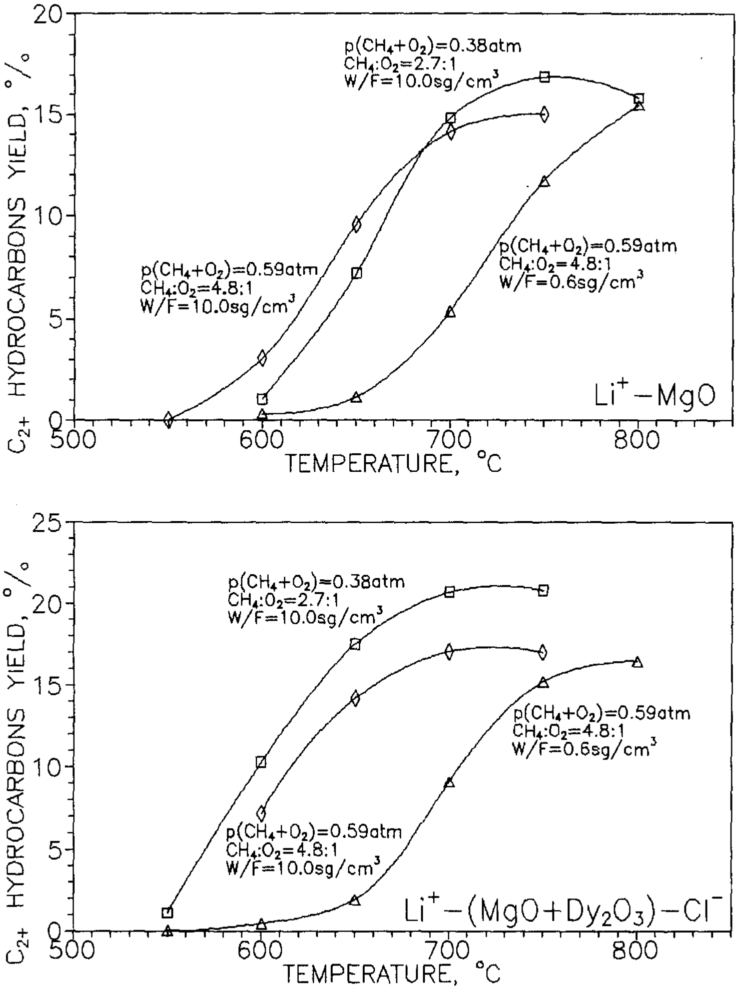

Fig. 3. Effect of reaction conditions on C_{2+} hydrocarbon yield.

for the activation of methane and the degree of its conversion is a factor of key importance for the course of the reaction.

According to the heterogeneous–homogeneous model and Eley–Rideal mechanism for the oxidative coupling of methane, the initial steps of the process may be expressed by the following equations [13–16]:

$$O_2(g) + 2s \rightleftharpoons 2O{-}s$$

$$CH_4(g) + O{-}s \rightarrow CH_3(g) + HO{-}s$$

(where s = active surface site). At the first step oxygen is dissociatively and reversibly adsorbed on the catalyst surface forming two active oxygen sites. It is assumed that O^- species are active oxygen sites. This surface bound oxygen, rather than oxygen from the gaseous phase, is involved in the CH_3 production. CH_3 radicals, in

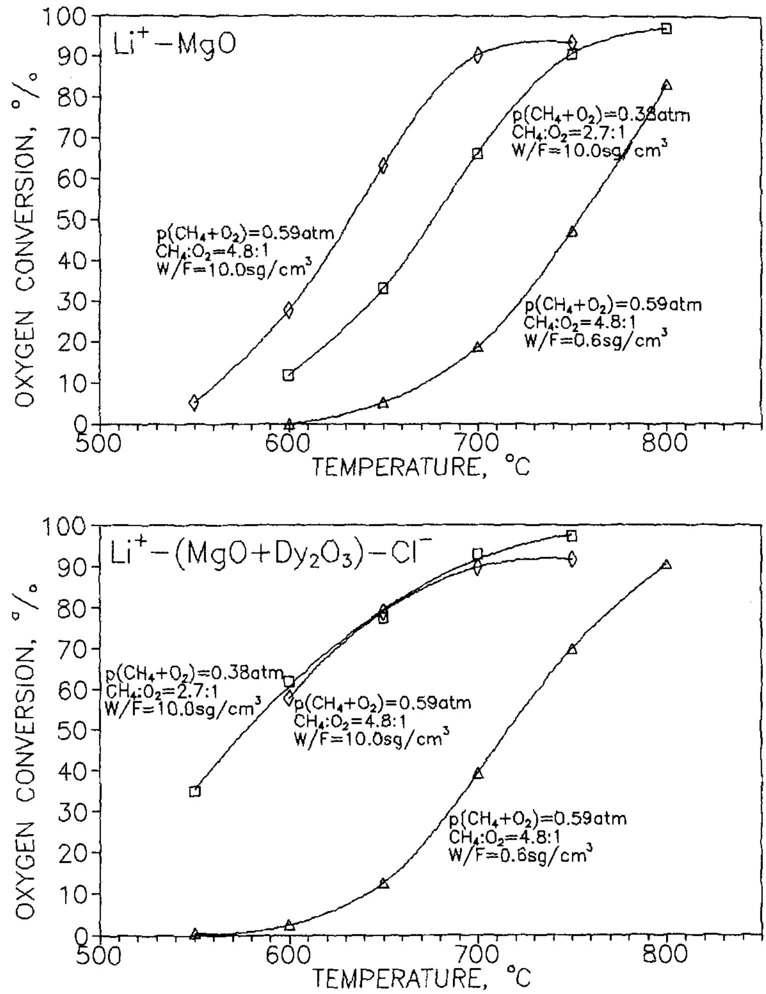

Fig. 4. Effect of reaction conditions on oxygen conversion.

turn, can undergo dimerization and form ethane and, on next steps, ethylene or they may undergo oxidation with the oxygen from the catalyst surface or from the gaseous phase and form carbon oxides.

At moderate temperatures (600–650°C), when a large amount of unreacted oxygen remains in the gaseous phase, low methane conversion may be caused by a small number of sites containing active oxygen on the catalyst surface. There may be various reasons for this situation:

(1) Active surface sites "s" are the sites of competitive adsorption of oxygen and carbon dioxide [17] and may be largely blocked by the adsorbed CO_2 formed during the process. More numerous sites are blocked at lower than at higher temperatures. This is indicated by the correspondence of the temperature range in question with the temperature of the beginning of carbon dioxide desorption with

Li^+–MgO [18–20]. Under the conditions of the reaction carried out at 600°C the time of CO_2 remaining on the surface of Li^+–MgO is long [21]. The slow removal of CO_2 from the surface and, hence, slow regeneration of sites "s" could constitute at such temperatures a step limiting the rate of active oxygen sites formation and, further on, the course of the whole process.

(2) Centres F, described as oxygen vacancies containing two electrons on surface sites with low coordination number, may be regarded as sites of active oxygen adsorption [22–24]. The number of these centres at temperatures below 700°C is very small and it increases rapidly only above that temperature.

(3) O^- species regarded as responsible for selective oxidative coupling of methane, at temperatures below 550–600°C exist in the form of a peroxy anion O_2^{2-} which thermally decomposes into O^- only above these temperatures [25]. At temperatures 600–650°C the number of formed O^- species is probably small. The peroxy anion O_2^{2-} itself is not able to allow the selective coupling of methane. Chang et al. [26] are of the opinion that the decomposition of the peroxy anion into O^- species may be enhanced by the presence of steam of which the concentration – since it is a reaction product – cannot be high with a low conversion degree.

With an extended time of the reaction mixture remaining in contact with the catalyst, the number of the reaction cycles occurring on a single active centre rises, thus increasing the conversion of both reagents and hydrocarbon C_{2+} yield which has been observed at moderate temperatures. A simultaneous increase of steam would then facilitate the removal of carbon dioxide [20] from the catalyst surface, thus increasing the number of sites available for oxygen adsorption which, in turn, allows a further increase in the conversion of the reagents. For the same reason the decomposition of ions O_2^{2-} to O^- should also be intensified. An additional effect of a higher steam concentration may be a desorption of any oxygen molecules from the catalyst surface which tend to produce carbon dioxide [27] and this may constitute one of the reasons for the improvement in the selectivity of hydrocarbon C_{2+} formation at temperatures below 700°C.

Another, more significant reason for the improved selectivity under moderate temperatures may be an increase in methane conversion. At low methane conversion a small amount of the formed CH_3 species does not create appropriate conditions for their contact and coupling – their oxidation seems more probable and becomes more important, thus decreasing the selectivity of hydrocarbon formation. In view of the low reaction rate at those temperatures, an increase in the W/F contact time makes possible a higher concentration of CH_3 species and, thus, also of the formed C_{2+} hydrocarbons.

Over Li^+–MgO at 600°C and $W/F = 0.6$ s g/cm^3, when oxygen conversion was almost zero, C_{2+} selectivity was much higher than that obtained under analogical conditions on Li^+–(MgO + Dy_2O_3)–Cl^-, on which, however, oxygen conversion was above zero. This seems to indicate that on Li^+–MgO the number of free sites of active oxygen adsorption is close to zero at that temperature and that CH_3 oxidation takes place on active surface oxygen rather than in a gaseous phase.

The higher conversions of oxygen and methane over Li^+–($MgO + Dy_2O_3$)–Cl^- indicate a larger number of O^- sites than on Li^+–MgO existing already at the temperature of 550°C. This suggestion seems to be supported also by the increase – in opposition to Li^+–MgO – in the conversion of the reagents at temperatures below 700°C after a decrease in both methane : oxygen ratio and their partial pressures.

At temperatures above 700°C there may exist a large number of free sites of active oxygen O^- which would enable an effective course of the reaction even with a short contact time. The extension of the latter in this temperature range contributes to an inversion (decrease) of the selectivity, most probably by oxidation not only of CH_3 but also of C_{2+} products to carbon dioxide.

The additional promoting with Dy_2O_3–Cl^-, employed by Lunsford [6], ensured an improvement in the properties of the catalyst, but even the primary Li^+–MgO, at moderate temperatures, can give a much better yield and selectivity if only the reaction takes place for a sufficiently long contact time, optimal for a given temperature. In study [28] it has been demonstrated that on Li^+–MgO methane conversion and hydrocarbon C_{2+} yield pass through a maximum while raising the W/F. Long contact times while operating at temperatures 600–650°C were also applied in studies with catalysts Li/MgO [26], $CaNiKO_x$ [3,4,7,11,12], LiCl–Na_2MoO_4 [29]. Most probably, various catalysts require various contact times, specific for them, at which – at a given temperature – the reaction of oxidative coupling of methane occurs with an optimal effectiveness. The better the catalyst, the shorter the contact time probably can be.

4. Conclusions

The presented results unequivocally indicate that the contact time of the reaction mixture with the catalyst constitutes a parameter which conditions an effective course of the reaction of methane oxidative coupling at moderate temperatures. A lowering of the reaction temperature requires, at least for some catalysts, a much longer contact time than those applied in a great majority of studies reported so far [15,16]. One may long look for a catalyst active and selective in a range of moderate temperatures but fail to find it because of inappropriate reaction conditions. But it may also turn out that the catalysts so far regarded as "high-temperature" catalysts can also work at lower temperatures when reaction conditions have been optimized.

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