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Oxidative coupling of methane over a sodium-calcium oxide catalyst modified with chloride ions

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Abstract

The paper presents results of systematic studies in the effects of a wide range of amounts of chloride ions introduced to the Na/CaO catalyst on the oxidative coupling of methane carried out in varied reaction conditions concerning a wide range of temperatures, oxygen concentrations and contact times of reagents with the catalyst. The positive influence of the presence of chloride ions is evident at their relatively small contents in the catalyst and specific effects depend mainly on the reaction temperature. There is an optimal content (about 2 wt.%) of chloride ions in Na/CaO, at which the total selectivity of reaction and selectivity of ethane formation reach the highest values, higher than those with the chloride-free catalyst. An improvement in the selectivity of ethylene formation is obtained only at higher reaction temperatures. Still, at every amount of chloride ions present in the catalyst, there may occur a decrease in its activity, especially at lower reaction temperatures. The operation of the chloride modifier consists in poisoning the catalyst surface and diminishing the number of sites with active oxygen, which results in excluding primarily the most active of these sites from methane transformations.

Keywords: Oxidative coupling of methane; Na/CaO catalyst; Chloride modifier; Activity; Selectivity

1. Introduction

The high and unstable prices of oil stimulate a re-examination of the process of oxidative coupling of methane (OCM) and its catalysts. Finding a selective catalyst, which would enable a replacement of oil with the natural gas to obtain ethylene still constitutes a great challenge.

In studies carried out so far, many kinds of potential catalysts of the OCM process have been applied, mainly alkaline-earth oxides, lanthanide oxides, transition metal oxides, etc., which were most frequently promoted with alkali metal ions [1–6]. In order to increase the selectivity of forming C_{2+} hydrocarbons (containing two and more carbon atoms in the molecule, mainly ethane and ethylene), additional promoters and modifiers were added to the catalysts. Chloride ions have proved to be promising modifiers of many kinds of OCM process catalysts, not only oxide-based. They were introduced into the catalyst already on the stage of its preparation, often together with an alkali metal promoter, e.g. LiCl or NaCl [7–12] or by employing materials containing chloride ions: oxychlorides [16,22], chlorinated precursors of perovskites [23] or chlorophosphates and chloroapatites [24], but also in the form of ammonium chloride or hydrochloric acid, as an additional modifier of catalysts obtained from chloride-free precursors [25,26,27]. Catalyst modification was also accomplished by adding chlorine [28], hydrogen chloride [25,28,29–31] or chlorine-containing gaseous compounds – alkane chlorides (mainly chloromethanes) [9,15,17,19,23,29,32–46] – to the stream of the main reagents. Although the influence of these compounds on the course of the gas-phase steps of the OCM could not be excluded with certainty, nevertheless it has been demonstrated that they undergo destructive adsorption [47], leaving chloride ions on catalysts, which changes the properties of the catalyst surface and has important effects on the OCM [19,25,29,39–44].

The literature data on the effects of applying a chloride modifier are however ambiguous and even contradictory.

According to some reports, the presence of chloride ions in the catalyst caused an increase in methane conversion [8,12,14,24–27], yield [12,14,27] and total selectivity of C_{2+} hydrocarbons formation [9,12,14,21,23,24,26,27]. A significant

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and promising effect of the OCM on catalysts containing chloride ions was an increase in the selectivity of ethylene formation [8,10,17,21,23,24,26], especially, the mutual relation of the ethylene and ethane concentrations in the products of the process [8,10,11,17,22,24–26]. The latter effect was attributed to the intensification of one of the important secondary stages of the OCM process, namely, the dehydrogenation of ethane. The effect of chloride ions on the stage of the dehydrogenation of ethane was very evident and was confirmed by independent studies in the process of oxidative dehydrogenation of ethane [10,20,25,48,49]. Such effects of the OCM process, on the whole, clearly positive were observed after the modification with chloride ions on catalysts Li/MgO [10,11,25,27], Bi_2O_3/MoO_3 [8], $BaCl_2/CaO$ [14], $CaCl_2$/calcium chloroapatite and $CaCl_2$/calcium chlorophosphate [24], M(alkali metal)-ZrO_2-Cl [17]. In the presence of Li/MgO [11] and Bi_2O_3/MoO_3 [8], modified with lithium chloride, the percent contents of eth ylene among C_2 hydrocarbons reached values close to 100%.

Yet, in a considerable number of studies [9,12,16,18, 19,21–23,27] one may find data which do not prove such a clearly positive effect of the chloride modifier—not all the indexes of the OCM process were higher (or at least unchanged) than on chloride-free catalysts. Although the presence of chloride ions in Li/SiO_2 increased the selectivity of the reaction, the amount of methane converted decreased [9]. A similar effect was also obtained on catalyst Na/MnMgO containing chloride ions when the yield of C_2 hydrocarbons decreased [19]. In the presence of LiCl/MgO, methane conversion and total selectivity were higher than on Li_2CO_3/MgO, but the selectivity of ethylene formation and the ethylene/ethane ratio on the former catalyst were clearly lower than on the latter one [16]. An improvement of all the indexes of the process was obtained only after an additional introduction of bismuth oxychloride to the composition of the catalyst. In study [23], chlorinated perovskites $BaTiO_3$ and $BaZrO_3$ ensured an increased selectivity to ethylene and total selectivity but they failed to change, and even decreased, the ethylene/ethane ratio, the degree of methane conversion and the yield of C_{2+} hydrocarbons. Oxychloride SmOCl made it possible to obtain a high ethylene/ethane ratio but with a lower methane conversion and lower total selectivity of the process than on Sm_2O_3 [22]. Lower methane conversion and lower yield of hydrocarbons C_{2+} were obtained on catalysts Li(or Na)-Na_2MnO_4 containing chloride ions [18]. The latter catalysts, in turn, allowed an unusually high selectivity to hydrocarbons C_3. In the presence of catalyst NaCl/CaO, the conversions of both reagents, methane and oxygen, were lower than with the application of other sodium compounds [21], with a positive effect of NaCl on an increase of the total selectivity of the process and the selectivity of ethylene formation. An increase in the ethylene/ethane ratio in the process products on such a catalyst became evident only with a fairly long contact time of the reagents. A long contact time was the necessary condition of obtaining a high ethylene/ethane ratio also in study [22]. Increased conversion of methane in the presence of catalysts $NaCl/MnO_x/SiO_2$ and $NaCl/PbO_x/SiO_2$, in comparison with analogous catalysts promoted with other sodium compounds, depended on the reaction temperature and the composition of the reaction mixture [12]. In study [27], above 1023 K the OCM effects on catalyst Li/MgO containing chloride ions were poorer than on the unmodified catalyst. The latter data imply that, for the products of the OCM process carried out on catalysts modified with chloride ions, a significant role is played by the conditions under which it is carried out.

Although less frequently, yet quite a negative effect of the presence of chloride ions on the activity and selectivity of catalysts of the OCM process was also observed. On catalyst $Na/CaO/MgAl_2O_4$ [13], promoted with sodium chloride, methane conversion, C_{2+} hydrocarbons yield and the selectivity of their formation were lower than on catalysts promoted with sodium phosphate, carbonate or sulphate, though they were higher than on the catalyst to which sodium was introduced in the hydroxide form. The kind of the sodium compound introduced to such catalysts had no significant effect on the ethylene/ethane ratio. The introduction of KCl instead of K_2CO_3 to MnO_x did not cause an increase in C_2 hydrocarbons yield, and only an addition of $CHCl_3$ in the feedstock demonstrated the advantages of the promoter (modifier) of KCl, increasing C_2 hydrocarbons yield with an unchanged yield of carbon dioxide [15]. Lower conversions of oxygen and methane, a lower yield of C_{2+} hydrocarbons and the selectivity of their formation, as well as practically unchanged selectivity to ethylene were obtained on NiO promoted with NaCl and CsCl [7]. A clearly higher conversion of methane and selectivity of ethylene formation were ensured only by chloride ions introduced to NiO in the form of LiCl.

The number of studies in which the OCM process was examined with catalysts containing chloride ions is much greater than those cited above but, because of lacking chloride-free standard catalyst, one can hardly evaluate the real effects that could be attributed to the presence of chloride ions.

Discrepancies similar to those reported above might be found in the literature data in which gaseous chlorine compounds were introduced into the reactor together with methane and oxygen. Undoubtedly, positive effects included higher selectivity of ethylene formation and ethylene/ethane ratio increased by chloromethanes and chloroethanes [9,15,17,19,23,25,28,29,32,33,36–40,42,43,45,46]. It was usually a quantitatively higher effect than that caused by chloride ions added directly to the catalyst. Such changes were usually accompanied by an increase of total selectivity and higher methane conversion. An analogous effect was also caused by hydrogen chloride added in large amounts to the methane–oxygen mixture [30,31]. In studies [17,29–31,33–35,37,38,42,44,46] the parameters that determined the direction of changes in the values of reagents conversion and process selectivity included: the kind of the catalyst, temperature and concentration of chlorine compounds in the feedstock. An addition of gaseous chlorine compounds was sometimes neutral [17,30,31,33,38,46] or even making worse some or all the effects of oxidative coupling of methane [29,33–35,37,38,42,44,46]. A negative consequence, such as a decrease in methane conversion and selectivity of ethylene formation, resulted also from an addition of gaseous chlorine to the feedstock [29].

It seems that discrepancies in the literature data which make it impossible to unequivocally estimate the usefulness of modifying catalysts of the OCM process with chloride ions, may result from a different nature of the examined catalysts, various amounts of chloride ions introduced to the catalysts and various reaction conditions under which the studies described above were carried out. In study [25], Lunsford et al. showed that a significant increase of methane conversion and ethylene/ethane ratio occurred only when Cl/Li atomic ratio in catalyst Li/MgO was close to unity (the effects of the OCM process in the presence of catalysts containing a higher amount of chloride ions were not examined in that study). The same Cl/Li ratio ensured the highest activity of Li/MgO also in the reaction of the oxidative dehydrogenation of ethane [20].

This paper presents results of systematic studies in the effects of chloride ions, introduced in a broad range of amounts to catalyst Na/CaO, on the products of the oxidative coupling of methane carried out in changeable – also in a wide range – reaction conditions, including temperature, oxygen concentration and contact times of the reagents with the catalyst. The aim of the study was to find out if chloride ions really constitute a positive modifier of one of the simplest and cheapest catalysts, yet which simultaneously exhibits good properties in the OCM process (e.g. refs. [1–6]), as well as to determine at which chloride ions amounts in the catalyst and under what conditions of the reaction one may expect positive effects of their introduction to the catalyst, and how large are these effects.

2. Experimental

The reaction catalysts were Na/CaO modified with chloride ions. They were obtained by impregnation of calcium carbonate (analytical grade, BDH Chemicals Ltd.) with aqueous solutions of sodium carbonate (analytical grade, POCh Gliwice, Poland) and appropriate amounts of ammonium chloride. After water evaporation, the formed pastes were dried at 383 K. Dry powders of catalyst precursors were pelleted and crushed to a grain size of the 0.75–1.2 mm. The catalysts were calcined in pure air (70 cm^3/min) at the temperature 1073 K for 1.5 h just prior to the beginning of the reaction. The nominal content of deposited sodium ions in all catalysts was 3 wt.% with respect to the weight of calcium oxide and the experimentally determined contents of the chloride ions in the calcined catalysts were varied from 0 to 11.08 wt.% (Table 1).

Table 1
Catalyst characterization results

Catalyst	Chloride ions content[a] (wt.%)	Surface area[b] (m^2/g)
Na/CaO	0	1.7
0.2Cl-Na/CaO	0.18	1.3
0.5Cl-Na/CaO	0.46	1.2
1Cl-Na/CaO	1.27	1.3
2Cl-Na/CaO	2.25	1.2
6Cl-Na/CaO	6.64	1.1
11Cl-Na/CaO	11.08	1.2

[a] Chloride ions contents determined by X-ray fluorescence spectroscopy (XRF).

[b] BET total surface area measured by argon adsorption at the liquid nitrogen temperature.

The contents of chloride ions in calcined catalysts were determined by X-ray fluorescence spectroscopy technique. Pellets for the XRF analysis were prepared by pressing catalysts powder. The measurements were performed by the energy-dispersive XRF spectrometer (Canberra) equipped with the liquid nitrogen-cooled Si(Li) detector. The AXIL software package was used for spectral deconvolution and for the calculation of the chloride ions content.

BET total surface area of the catalysts in their oxide form (after calcination) was measured by argon adsorption at the liquid nitrogen temperature in a static-volumetric glass apparatus, which ensured a vacuum better than 2×10^{-6} kPa.

X-ray powder diffraction patterns of calcined catalysts were collected with an upgraded Zeiss HZG-4 diffractometer using Ni-filtered Cu Kα radiation. The samples were scanned by a step-by-step technique, at 2θ intervals of 0.05° and recording time of 10 s for each step. The measured patterns were compared with the JCPDS (Joint Committee on Powder Diffraction Standards) database for phase identification.

The reaction of oxidative coupling of methane was carried out in a single pass of the reaction mixture through the quartz flow reactor. An internal diameter of the reactor was 10 mm and behind the catalyst layer was narrowing down to 3 mm. Such construction of the reactor enabled a rapid acceleration of the linear rate of gas flow to limit to a minimum the possibility of secondary transformations of the reaction products beyond the catalyst. The amount of the catalyst (W) in the reactor was 0.5 g. The catalyst was mixed with quartz (0.75–1.2 mm grains) at the ratio of 1:10 to warrant the constant temperature in the catalytic layer. The reaction temperature, measured in the centre of the catalyst + quartz bed, was adjusted from 973 to 1123 K. The content of oxygen in the methane + oxygen mixture was 4.76 vol.% (the methane/oxygen ratio equalled 20/1) or 9.09 vol.% (the methane/oxygen ratio equalled 10/1). The volumetric flow rate of the reaction mixture (F) was 75 or 150 cm^3/min. The modified contact time W/F was 0.4 or 0.2 s g/cm^3. All effects of the OCM process were collected at 0.5 h on-stream at the specified reaction conditions.

The analysis of the reaction mixture and the reaction products were performed by means of gas chromatography on Porapak Q (all hydrocarbons and carbon dioxide) using FID and TCD detectors coupled in series, and on molecular sieve 4A + 5A (oxygen) employing TCD detector. In none of the experiments carbon monoxide in the reaction products was detected. Chromatographic calibration was carried out with the standard mixtures containing hydrocarbons and other gases, whose concentrations were comparable with those analysed. The oxygen and methane conversions were calculated on the basis of their concentrations before and after the reaction, with a correction introduced for the change in gas volume during the reaction [50]. The same correction was applied in calculations of the methane conversion to the specific reaction products, i.e., the reaction selectivity. The carbon mass balance was found to be close to 100 ± 2%.

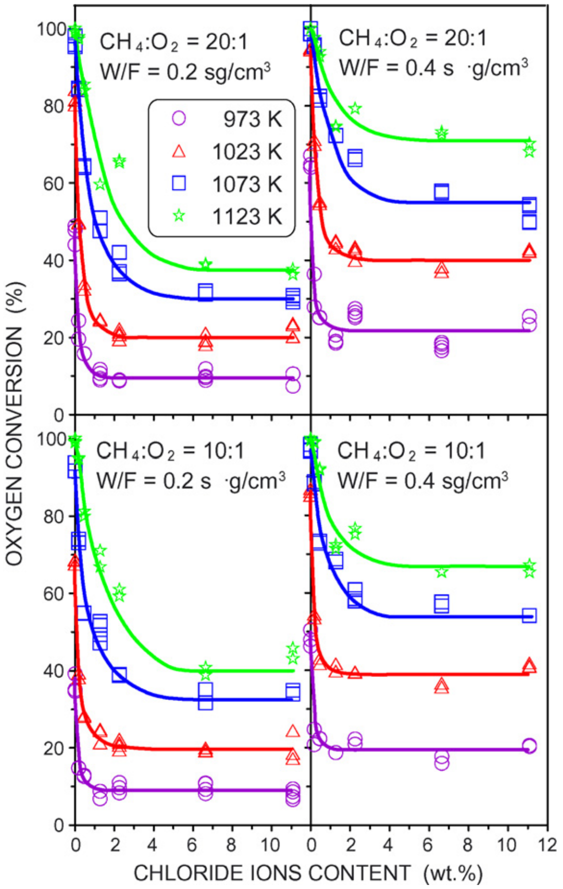

Fig. 1. Effect of chloride ions in Na/CaO catalyst on the oxygen conversion in the oxidative coupling of methane.

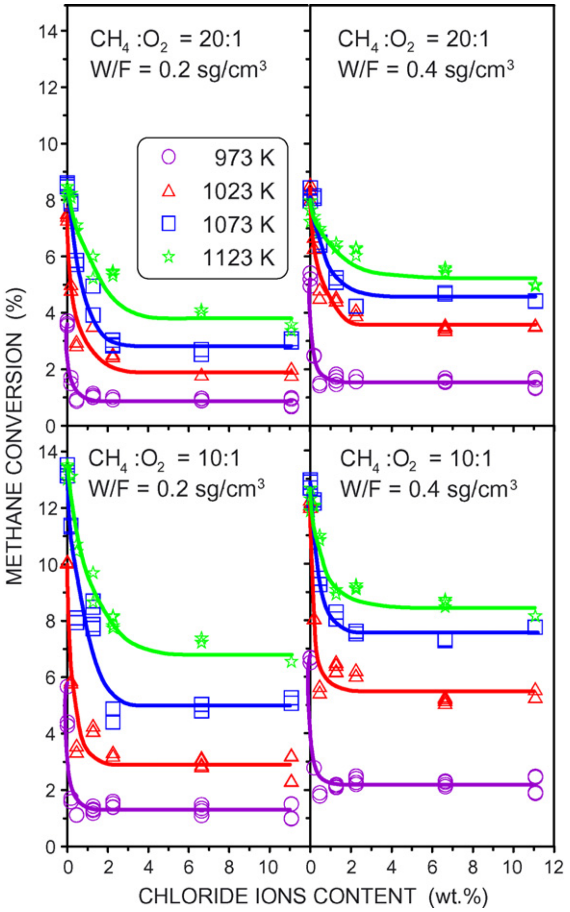

Fig. 2. Effect of chloride ions in Na/CaO catalyst on the methane conversion in the oxidative coupling of methane.

3. Results

An introduction of a chloride modifier to catalyst Na/CaO caused a decrease in its activity in comparison with the unmodified catalyst which was manifested as a decrease in the conversions of both reagents (Figs. 1 and 2). The decrease in the conversion of both methane and oxygen was the deepest after the introduction of small amounts of chloride ions. At lower temperatures of the process, their small amount was already sufficient to lower the activity, about 1 wt.% of Cl^- at 973 K, than at higher temperatures, about 4–5 wt.% of Cl^- at 1123 K (Figs. 1 and 2). Greater amounts of the modifier caused no further changes in the level of the conversion of both reagents.

The value of the decrease in oxygen conversion (Fig. 1) depends on the conditions of the process of oxidative coupling. The lower the temperature of the process and the shorter the contact time of the reaction mixture with the catalyst, the more significant the decreases in oxygen conversion caused by the presence of the chloride modifier. Thus, for instance, at 973 K, contact time 0.2 s g/cm^3 and reagents ratio CH_4:O_2 = 20:1, oxygen conversion decreases five times in comparison with the “clean” catalyst Na/CaO (from the level of 50 to 10%). On the other hand, at the same temperature and the same oxygen content in the reaction mixture, but with a longer contact time (0.4 s g/cm^3), the degree of oxygen conversion decreases only about three times (from the level of 65 to 20%).

In the case of the other reagent, methane, at the lower of the applied temperatures the value of the conversion decrease in the presence of chloride ions practically did not depend on the other reaction conditions—by about 75 relative percent (Fig. 2). On the other hand, at higher temperatures a significant role is also played by the contact time: at 1123 K and at $W/F = 0.2$ s g/cm^3, methane conversion decreases by about one-half (e.g. from 13.5 to 7% when the ratio CH_4:O_2 was 10:1), and at $W/F = 0.4$ s g/cm^3 only by about 30 relative percent (e.g. from 12.5 to 8.5% at the ratio CH_4:O_2 = 10:1).

A similar effect of chloride ions was observed in the case of the yield of C_{2+} hydrocarbons formation (Fig. 3). The most rapid drop in the yield was observed in the presence of small amounts of chloride ions (till about 2 wt.%), especially at lower temperatures of the coupling process. This fall was about 70 relative percent, regardless of the contact time and oxygen concentration in the reaction mixture. At the temperature of 973 K, the highest yield of hydrocarbons C_{2+}, on the level of 4.8%, was obtained with the contact time $W/F = 0.4$ s g/cm^3 and the ratio CH_4:O_2 = 10:1, while the lowest yield of 3% was obtained at $W/F = 0.2$ s g/cm^3 and CH_4:O_2 = 20:1. Along with the rise of the temperature of the process, the presence of chloride ions in the catalyst caused smaller and smaller changes in the yield

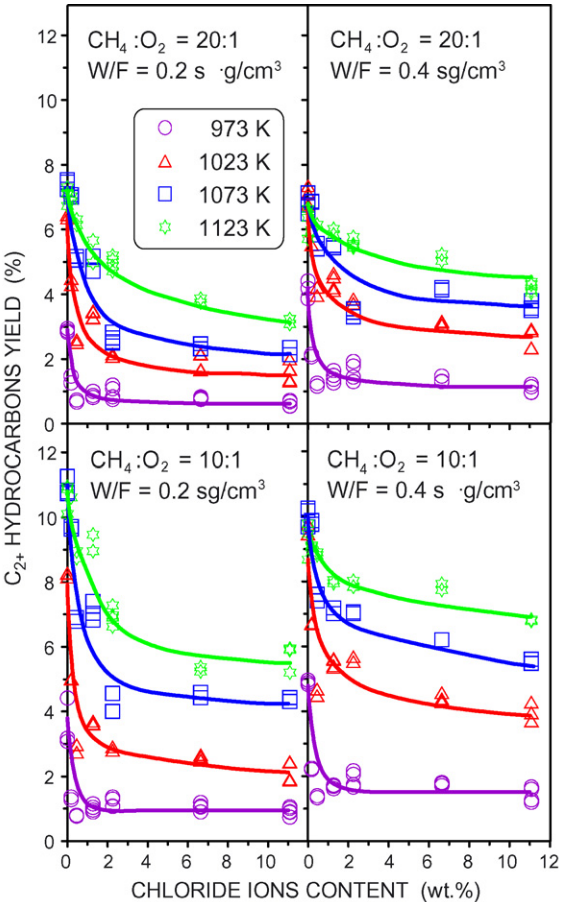

Fig. 3. Effect of chloride ions in Na/CaO catalyst on the C_{2+} hydrocarbons yield in the oxidative coupling of methane.

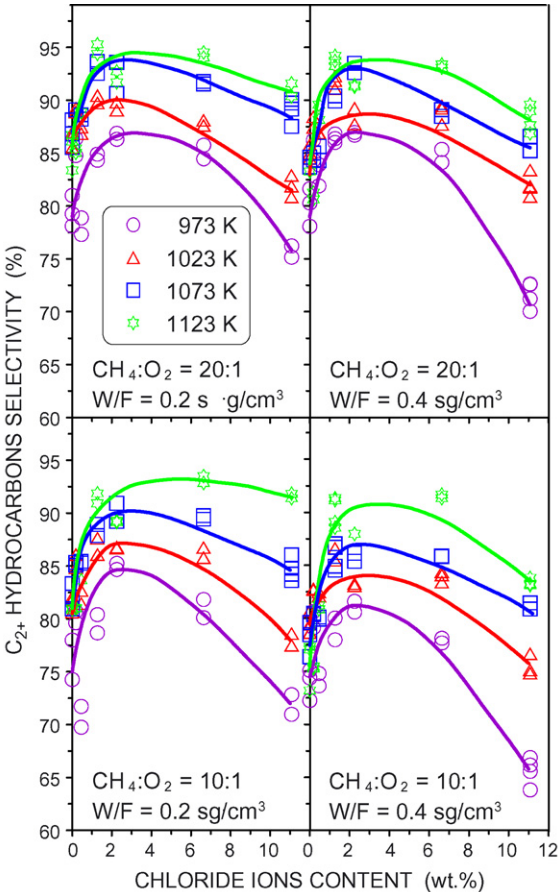

Fig. 4. Effect of chloride ions in Na/CaO catalyst on the C_{2+} hydrocarbons selectivity in the oxidative coupling of methane.

of hydrocarbons C_{2+} in comparison with unmodified catalyst Na/CaO. The smallest decreases in the yield were caused by the chloride modifier at the temperature of 1123 K, when at the contact time $W/F = 0.2$ s g/cm^3 the yield decreased by a half, and at a longer contact time, $W/F = 0.4$ s g/cm^3, by about 30 relative percent. At this temperature, the highest yield of hydrocarbons C_{2+} was observed at $W/F = 0.2$ s g/cm^3 and CH_4:O_2 = 10:1 on catalyst Na/CaO and it was 11%.

The effect of the chloride modifier on total selectivity of C_{2+} hydrocarbons formation, which includes selectivities to the main hydrocarbons (ethane and ethylene) and C_{3+} hydrocarbons, was different (Fig. 4) from the observed effect on the degrees of the conversion of the reagents and hydrocarbons yield. Already small amounts of chloride ions (up to about 2 wt.%) caused a considerable increase of the selectivity. When the higher is the temperature of the oxidative coupling of methane, the increase is higher. At the temperature of 973 K, the increases in total selectivity were about 10 relative percents, regardless of the employed conditions of the reaction. The highest values of the selectivity, on the level of 87% on catalyst 2Cl-Na/CaO, were observed at both applied contact times and at the lower oxygen content in the reaction mixture (CH_4:O_2 = 20:1). Larger amounts of the chloride modifier (above 2 wt.%) increased the total selectivity to a smaller extent. At a high, 11% content of chloride ions, the total selectivity of the process drops below the value characteristic of chloride-free catalyst. Along with the increase in the temperature of the OCM process, the values of total selectivity were higher and higher, whereas its increases caused by the addition of chloride ions to catalyst Na/CaO remained on the level of about 10 relative percent. The highest selectivity of the formation of all hydrocarbons, on the level of 95%, at the temperatures of 1073–1123 K, was obtained on catalyst 2Cl-Na/CaO at the CH_4:O_2 ratio of 20:1. Also at these temperatures, the presence of chloride ions in amounts over 2 wt.% causes smaller increases in the values of the selectivity, yet it was always higher than that obtained on “pure” catalyst Na/CaO.

Changes in the selectivity of the formation of ethane, which take place after the introduction of chloride ions to catalyst Na/CaO are very similar to those in total selectivity. The selectivity of the formation of ethane (Fig. 5) increases after the addition of small amounts, up to 2 wt.%, of the chloride modifier. For example, with the contact time $W/F = 0.4$ s g/cm^3 and the CH_4:O_2 ratio of 20:1 and at the temperature of 973 K, the selectivity of the formation of ethane rises by about 20%, from 58 to 77%, while at the temperature of 1123 K and other conditions remaining the same the selectivity rises from the level of 37–42%. The contents of the chloride modifier higher than 2 wt.% caused a decrease in the selectivity of the formation of ethane in comparison to that characteristic of the catalyst 2Cl-Na/CaO. The decrease in the selectivity is smaller at higher

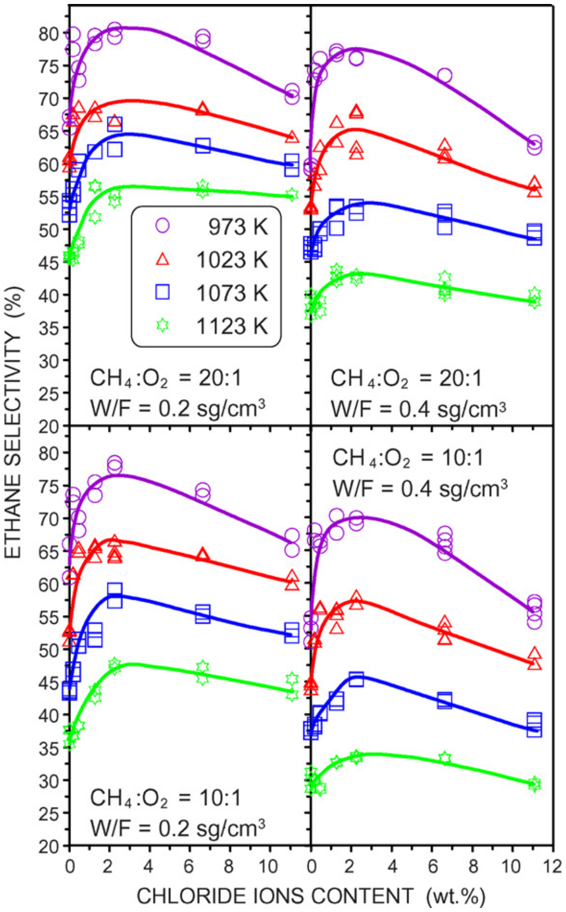

Fig. 5. Effect of chloride ions in Na/CaO catalyst on the ethane selectivity in the oxidative coupling of methane.

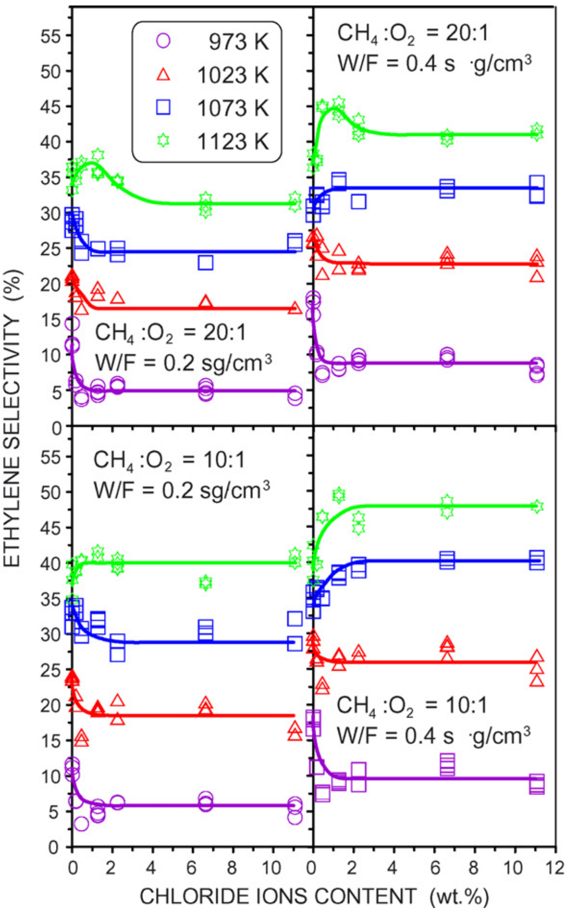

Fig. 6. Effect of chloride ions in Na/CaO catalyst on the ethylene selectivity in the oxidative coupling of methane.

temperatures, and the selectivity obtained on catalyst 11Cl-Na/CaO – under none of the applied reaction conditions – was lower than that obtained on the unmodified catalyst Na/CaO. The value of the selectivity of the formation of ethane was also affected by the contact time and oxygen concentration in the reaction mixture. On catalysts modified with chloride ions, higher values of the selectivity were obtained with shorter contact times and lower oxygen contents. In all of the applied reaction conditions, the highest selectivity was obtained on catalyst 2Cl-Na/CaO; for instance, at 973 K and the reagents ratio of CH_4:O_2 = 20:1 and $W/F = 0.2$ s g/cm^3, it was 80%, while at $W/F = 0.4$ s g/cm^3, it was 77.5%. At the temperature of 1123 K and the same ratio of the reagents the selectivity of the formation of ethane was 55% with $W/F = 0.2$ s g/cm^3, while with $W/F = 0.4$ s g/cm^3 it was 42.5%.

The influence of chloride ions on all results of the OCM process discussed so far was uniform, i.e., under all the reaction conditions they caused either an increase in the value or its decrease, or there occurred a maximum at about 2 wt.% contents of chloride ions. In the case of the selectivity of the formation of ethylene (Fig. 6), the influence of the modifier was more complex and it significantly depended on all the conditions of the reaction of the coupling process. Regardless of the other reaction conditions, at the temperatures of 973 and 1023 K, the addition of chloride ions in the amount of 1–2 wt.% to the catalyst Na/CaO caused a decrease in the selectivity of the formation of ethylene to a level which remained constant also at higher contents of the modifier. The deepest decreases were observed at the temperature of 973 K, e.g. with $W/F = 0.4$ s g/cm^3 and CH_4:O_2 = 10:1, after an introduction of 2 wt.% of chloride ions the selectivity decreased from 17.5 to 9%. At the temperature of 1073 K, the influence of chloride ions depends on the contact time of the reaction mixture with the catalyst. With a shorter contact time, $W/F = 0.2$ s g/cm^3, the influence of the added modifier was the same as at lower temperatures—a small amount of the modifier caused a decrease in the selectivity of the formation of ethylene. On the other hand, with a longer contact time, $W/F = 0.4$ s g/cm^3, the presence of the modifier in amounts up to 2 wt.% caused an increase in the selectivity and a greater increase in the formation of this hydrocarbons was observed at a higher content of oxygen in the reaction mixture. Under such conditions, the selectivity rises from 34 to 40%. Still greater amounts of chloride ions do not cause any further changes in the value of the selectivity. At the temperature of 1123 K, the direction of changes in the selectivity of the formation of ethylene also depends on the concentration of oxygen in the reaction mixture. With the ratio of the reagents CH_4:O_2 = 10:1, small amounts of chloride ions increase the selectivity of the formation of ethylene. This increase is much larger in the case of a longer contact time—from 39% on Na/CaO to 48% on modified

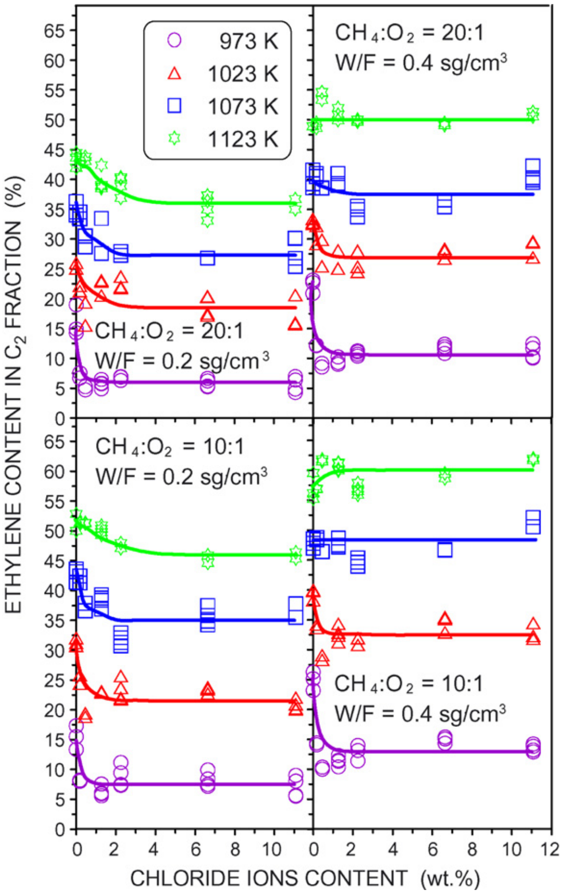

Fig. 7. Effect of the chloride ions introduced into Na/CaO catalyst on the percent content of ethylene in the sum total of hydrocarbons C_2 in the reaction products.

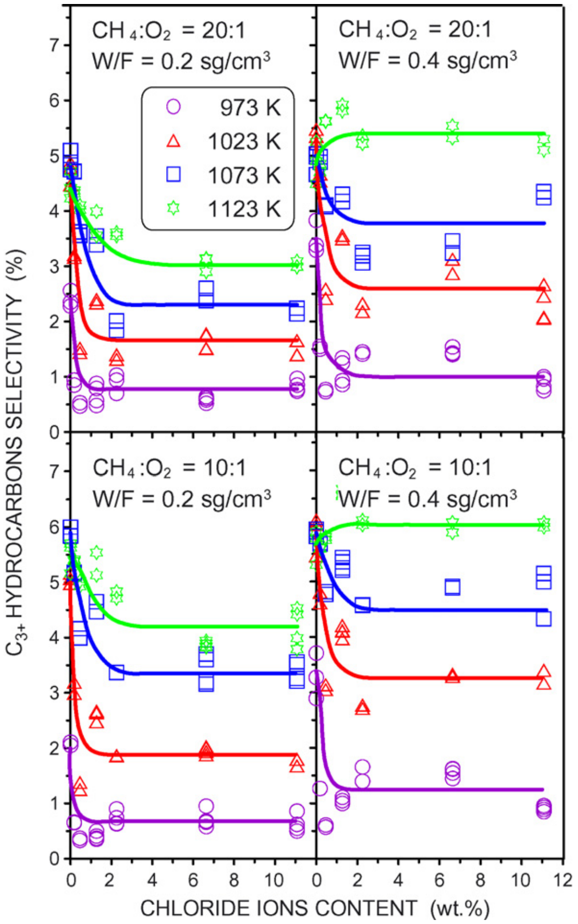

Fig. 8. Effect of chloride ions in Na/CaO catalyst on the C_{3+} hydrocarbons selectivity in the oxidative coupling of methane.

catalysts containing 2 wt.% and more of chloride ions. With the ratio of the reagents CH_4:O_2 = 20:1, chloride ions also increase the selectivity of the formation of ethylene but in this case a clear peak in the selectivity was observed at 1% content of chloride ions; with $W/F = 0.2$ s g/cm^3, it was on the level 37.5% and with $W/F = 0.4$ s g/cm^3 the maximum selectivity reached the value of 45%. In the case of the shorter contact time, the modifier in the amount above 2 wt.% caused a drop in the selectivity to ethylene below the value obtained on the chloride-free catalyst Na/CaO.

The large increase in the selectivity of the formation of ethane with simultaneous multidirectional changes in the selectivity of the process to ethylene cause that the percent content of the latter hydrocarbon in fraction C_2 is generally smaller in the presence of modified catalysts than with chloride-free catalyst Na/CaO (Fig. 7). At the temperature of 973 K, at which in the presence of Na/CaO ethylene content in the sum total of C_2 hydrocarbons is already small, below 25%, even very small amounts of chloride ions decrease it still further by one-half. Raising the temperature of the OCM process causes that the decrease in the percent content of ethylene is smaller. At high temperatures of the reaction, but only with a longer contact time, the presence of chloride ions in the catalyst is neutral for the percent participation of ethylene in the fraction of C_2 hydrocarbons or, as at 1123 K and $W/F = 0.4$ s g/cm^3, it causes its slight increase. With the ratio of the reagents CH_4:O_2 = 20:1 there occurs a clear peak of ethylene content with catalyst 0.5Cl-Na/CaO, whereas when the CH_4:O_2 ratio was 10:1 also larger amounts of chloride ions increased the percent content of ethylene. With that most advantageous set of reaction conditions the C_2 hydrocarbons fraction formed on Na/CaO contained 57% of ethylene, while the modification of the catalyst with chloride ions increased its content to 60%.

Apart from ethane and ethylene among the hydrocarbons formed in the process of oxidative coupling of methane, there are also C_{3+} hydrocarbons (propane, propylene and C_4 hydrocarbons). The selectivity of the conversion of methane to this group of hydrocarbons is usually very small. In the experiments described in this paper, it was always below 6%. The presence of the chloride modifier in catalyst Na/CaO decreases the selectivity of the formation of C_{3+} hydrocarbons almost under all conditions (Fig. 8). The chloride modifier in the amount of up to 2 wt.% very rapidly decreases the selectivity to C_{3+}, while its larger amounts caused no further changes in this selectivity. Only at the temperature of 1123 K and contact time $W/F = 0.4$ s g/cm^3, regardless of oxygen concentration in the reaction mixture, were the results of the OCM process different: under such conditions a slight increase in the selectivity to C_{3+} in comparison with unmodified catalyst Na/CaO was observed.

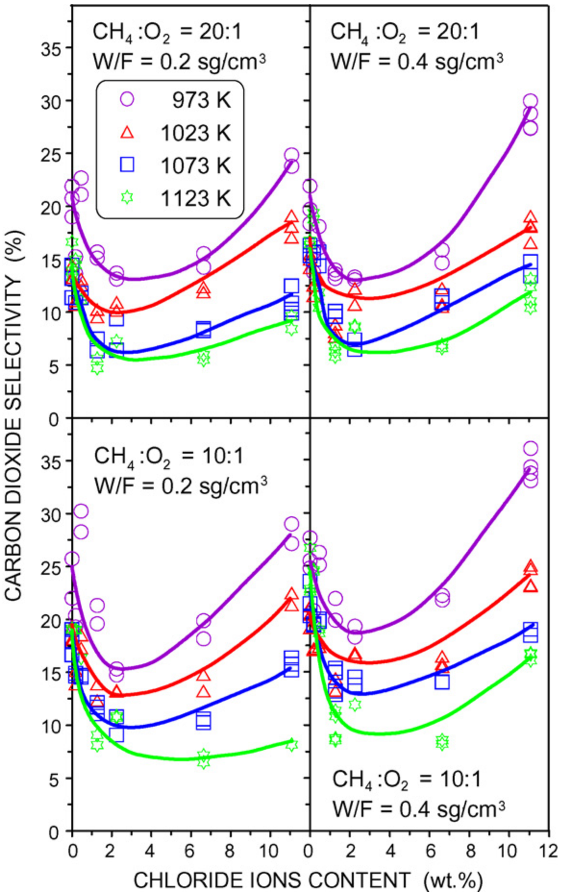

Fig. 9. Effect of chloride ions in Na/CaO catalyst on the carbon dioxide selectivity in the oxidative coupling of methane.

Another product of the OCM process is also carbon dioxide. Chloride ions present in the catalyst Na/CaO in small amounts, up to 2 wt.%, considerably limit complete oxidation of hydrocarbons to CO_2 (Fig. 9). Greater amounts of the modifier, above 2 wt.%, again intensify the participation of the complete oxidation of hydrocarbons, whose result is an increase in the selectivity of the formation of CO_2. The values of the selectivity of the formation of carbon dioxide complement the total selectivity of the formation of hydrocarbons C_{2+} to 100%, and the dependences shown in Fig. 9 constitute a mirror reflection of those shown in Fig. 4 and thus do not require a more detailed presentation. Nevertheless, one should stress that the participation of the processes of complete oxidation with catalysts modified with chloride ions is very small; with catalysts 1Cl-Na/CaO and 2Cl-Na/CaO, this undesirable product is formed only from 5 to 10% of reacted methane.

4. Discussion

Figs. 1–9 show that the evaluation of the influence of the chloride modifier of catalyst Na/CaO on the products of the oxidative coupling of methane must depend both on its content in the catalyst and on all the parameters of the reaction, such as temperature, oxygen concentration in the methane–oxygen feedstock and its time of contact with the catalyst. Only the role of chloride ions is unequivocally negative in determining the activity of the catalyst—the value of the conversion of both reagents, at every contents of the chloride modifier, is always lower than with the unmodified Na/CaO (Figs. 1 and 2). At the lower temperature of the process, 973 K, there occurs a deep drop in the conversion of oxygen and methane already in the presence of very small amounts of chloride ions. Only at 1073–1123 K is the decrease in the activity less rapid and smaller at analogous contents of the modifier. An evidently positive effect caused by the chloride modifier is an increase of the total selectivity of the OCM process at each temperature, at each composition of the reaction mixture, and with each time of its contact with the catalyst (Fig. 4). Yet, this is true only about small amounts of chloride ions. There is an optimum contents of chloride ions in the catalyst, about 2 wt.%, at which the increase in the selectivity of the formation of C_{2+} hydrocarbons is the largest in comparison with the value obtained with the chloride-free catalyst. This increase in the selectivity of the process towards C_{2+} hydrocarbons causes that in the presence of the modified catalysts their yield does not drop so rapidly and greatly (Fig. 3) as the decrease in methane conversion seems to suggest. The selectivity of the formation of the most desirable product of the OCM, i.e., ethylene, is only slightly improved at some conditions of the reaction namely, at a high temperature of 1123 K and – with a longer contact time – also at 1073 K (Fig. 6). Previously [21], a clear increase in the selectivity of the formation of ethylene and the ratio of ethylene/ethane with a similar catalyst NaCl/CaO, in comparison with calcium catalysts promoted with other sodium compounds, was obtained at 1023 K only with a very long contact time W/F close to 4.4 s g/cm^3. Thus, catalyst Na/CaO modified with chloride ions, though only with their optimum contents of about 2 wt.%, may be recommended only for a high-temperature process of oxidative coupling of methane carried out with a fairly long time of contact of the reagents with the catalyst, longer than in the case of unmodified Na/CaO. Oxygen concentration in the reaction mixture may then be increased (within the range allowed by the explosion limit), which would ensure a greater yield of C_{2+} hydrocarbons and simultaneously high general selectivity and selectivity of the formation of ethylene. The longer time of contact of the reaction mixture with the catalyst and higher contents of oxygen favour the successive reaction in a series of intermediate stages of the OCM process, i.e., oxidative dehydrogenation of ethane.

To some extent, the lower activity of catalysts modified with chloride ions may result from their smaller surface area in comparison with the surface area of the chloride-free catalyst. Still, this characteristic of the modified catalysts cannot be the only cause of the gradual loss of activity and complex changes of the selectivity of the process which take place when chloride ions content changes; the value of the surface area of all these catalysts is practically the same (Table 1).

The most probable cause of the modifying action of chloride ions is the poisoning of the catalyst surface by them and decreasing the number of sites with active oxygen. In consequence, there decreases the rate of all the stages of the process taking place with its participation, i.e., the activation of methane, which is manifested as a decrease in the degree of the conversion and successive transformations of hydrocarbons leading up to their complete oxidation. Already very small amounts of chloride ions poison the most active sites on the catalyst surface containing oxygen at which there occur first of all processes of the full oxidation of hydrocarbons. A similar suggestion may be found in study [17]. It was also noted that chloride ions neutralize the strong basicity of the surface of catalysts Li/MgO [25,27], Na/CaO [21], $BaCl_2$/CaO [14] or Na/MnMgO [19]. In catalyst Li/MgO, small amounts of chloride ions are preferentially sited at low coordinate sites [51] and an analogous localization of chloride ions may be expected in catalyst Na/CaO. Study [52] reported a lower activity of chloride-modified catalyst in comparison with "pure" Na/CaO in the reaction of complete oxidation of methane (2 vol.% methane in air). In the OCM process, apart from reduction of the number of activated molecules of methane and observed value of the degree of methane conversion, the consequence of the decrease of surface concentration of sites containing the active form of oxygen is a decrease of the participation of complete oxidation of hydrocarbons to carbon dioxide, increase of the selectivity of the formation of C_{2+} hydrocarbons, including ethane, the primary reaction product and at higher temperatures also ethylene.

Chloride ions may also poison those sites on the catalyst surface, which contain less active oxygen, at which there are formed first CH_3 radicals and then C_2 hydrocarbons. Increasing the content of the modifier gradually poisons sites of lower activity, leading to ever lower conversion of both reagents and ever lower yield of the products of the OCM process. The intrinsic activity of Li-MgO-Cl catalysts for CH_3 radicals generation was lower than that of a normal Li-MgO catalyst [25]. A high concentration of chloride ions probably causes no further blocking of surface active sites but creates new sites at which there occurs complete oxidation of methane and ethane and of radicals formed from them—this is implied by the decrease in the selectivity of the reaction towards ethane (and of total selectivity) and a constant level of selectivity towards ethylene and C_{3+} hydrocarbons. At high contents of the modifier, there are formed even separate crystallographic phases of chlorinated calcium compounds. XRD examinations showed the presence of CaClOH (JCPDS 36-983) in catalyst 11Cl-Na/CaO. A much smaller amount of this phase and its high dispersion did not allow the demonstration of its presence (nor of crystallographic phases containing sodium ions) in modified catalysts containing smaller amounts of chloride ions. Large content of chloride ions may cause the recrystallization of all the other components of the catalyst and their segregation in separate, strongly dispersed crystallographic phases. In such a situation, the phase of calcium oxide may contain few (or none) sodium cations. Since it is sodium ions, incorporated into the lattice of calcium oxide constitute the most selective sites $\{Na^+–O^-\}$ [1–5], enabling the formation of CH_3 radicals from methane and then of C_2 hydrocarbons from them, the selectivity of the formation of ethane, ethylene, C_{3+} hydrocarbons and thus, the total selectivity of the process of oxidative coupling of methane in the presence of catalysts containing large amounts of the chloride modifier, is smaller than at their optimal contents, i.e., about 2 wt.%.

The very rapid and deep decrease in the activity of the modified catalysts at lower temperatures may result from the fact that under such conditions the dominant participation in the course of the process of the oxidative coupling of methane must belong to the most active sites on the catalyst surface. Their poisoning with small amounts of chloride ions practically stops the reaction of methane with oxygen. At higher temperatures, at which the reaction also occurs on the less active sites, still unpoisoned with the small amount of the modifier added to the catalyst, the observed decrease of the conversion of both reagents and hydrocarbons yield is small. Only the poisoning of also those less active sites with large amounts of the modifier considerably inhibits the course of the OCM process also at higher temperatures. It seems that at high temperatures of the reaction, the surface concentration of the active form of oxygen is still sufficiently high to enable the possibility of intensive secondary transformations of ethane to ethylene and, on subsequent stages, to hydrocarbons C_{3+}.

It is worth noticing that the optimum contents of about 2 wt.% of chloride ions in catalyst Na/CaO, corresponding to the atomic ratio Cl/Na equal to 0.85, is close to that established by Lunsford et al. for catalyst Li/MgO used in the reactions of the oxidative coupling of methane [25] and oxidative dehydrogenation of ethane [20]. So, it is possible to state that alkali metal and chloride ions should coexist in the optimal proportion on the catalyst surface to achive the high selectivity of the oxidative coupling of methane process.

The possible, disadvantageous aspect of the catalyst modification with chloride ions may be their slow "escape" from the catalyst during the OCM long-lasting process. Such phenomenon was already mentioned in some previous papers [8,16,22,24,25]. Some potential reasons for the lose of chloride ions are for example their reaction with oxygen (with gaseous chlorine as a product) and at subsequent stages, reactions of chlorine with water vapour and oxygen leading to hydrogen chloride. In the presence of sodium promoter a fraction of its chlorides may cover the catalyst surface. Because of the relatively low melting point of NaCl (1074 K), the reaction between the melt and water vapour may increase the amount of hydrogen chloride liberated at high temperatures of the OCM. The latter chlorine-containing product may also be formed directly in the reaction of surface chloride ions with methane. Those undesirable reactions are not very rapid but during the long-lasting OCM process they may affect the content of chlorides in the catalyst. In order to prevent diminishing in amounts of chloride ions in the catalyst, the continuous addition of gaseous chlorine-containing compounds in their very small concentrations to the methane–oxygen feedstock may be recommended. It should allow some chloride ions to be deposited on the catalyst [47] and replace the lost chlorides, maintaining their optimal amounts on the catalyst surface.

5. Conclusions

The results of the presented studies have shown that only small amounts of chloride ions introduced into catalyst Na/CaO may be recommended for an improvement of the effects of oxidative coupling of methane. There is an optimum contents of chloride ions in catalyst Na/CaO—about 2 wt.%. At this content of the modifier, the selectivities of the formation of ethane, ethylene and C_{3+} hydrocarbons, which all constitute the total selectivity of the process, reach the highest values, higher than those obtained with chloride-free catalyst; the complete oxidation of hydrocarbons to carbon dioxide is maximally restricted. But after such a modification of the catalyst, the OCM process must be carried out at higher temperatures. The other conditions of the reaction should also contribute to the course of the oxidative coupling of methane on less active sites of the surface—oxygen concentration in the reaction mixture should be high (within the range allowed by the explosion limit) and its time of contact with the catalyst should be longer than in the case of unmodified Na/CaO. The latter parameters are especially important for the formation of ethylene.

The role of the chloride modifier seems to consist in poisoning the catalyst surface and decreasing the number of sites with active oxygen, which in consequence leads mainly to an exclusion of the most active of these sites from methane transformations.

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