Oxidative coupling of methane over KCl–LnCl₃ eutectic molten salt catalysts

Joaquim B. Branco, Ana C. Ferreira, Ana M. Botelho do Rego, Ana M. Ferraria, Gonçalo Lopes, Teresa Almeida Gasche

1. Introduction

The activation of methane is, from both academic and environmental point of views, an important chemical topic. Among other reactions, the oxidative coupling of methane (OCM) is a one-step suitable catalytic route for the production of ethylene and ethane. However, the stability and deactivation of the catalysts are still today a major problem; namely over nickel based catalysts.

Many research groups continue to study the catalytic decomposition of N₂O [1–10] or its catalytic reduction by reagents such as hydrocarbons [11–20] or ammonia [21–23]. Using N₂O as starting feedstock, the activation of CH₄ and the elimination of N₂O can be simultaneously achieved with the formation of valuable chemical products such as C₂ hydrocarbons or synthesis gas. However, due to the relatively low emissions of N₂O compared to the demand of C₂ hydrocarbons (especially ethylene) the implementation of a sustainable industrial process for the production of hydrocarbons based on this reaction is not expected in a near future [24–28]. Instead, the importance of using N₂O instead of O₂ as oxidant agent for the activation of methane justifies the development of an environmentally viable solution since N₂O is recognized as a major greenhouse agent.

Strong acidic inorganic compounds are among the most active, selective and stable catalysts for the activation of CH₄ using N₂O as oxidant [12,29–34]. On the other hand, applications of molten salts are well recognized for more than a century and in spite of the use of high temperature corrosive liquids, molten salts offer unique opportunities [35]. Among them, acidic alkali molten metal chlorides appear as a “new” and challenging group of catalysts for numerous applications [35]. The molten salts can act not only as catalysts but, they can be used also as an active medium that disperse other catalytic active complexes. Molten salt catalytic properties are mainly linked to the high mobility of cations and anions within the melt that, reducing the interaction between different species allows the modulation of highly specific catalysts [36]. Therefore, molten salts can be used as an attractive and viable alternative to the classical catalysts used for the OCM process.

In our group, we have been studying the catalytic behavior of bimetallic oxides containing fblock elements using binary intermetallic compounds LnCu₂ (Ln = La, Ce, Pr, Eu, Gd, Dy, Tm) [37], LnNi (Ln = Pr, Gd, Lu), ThCu₂ and AnNi₁₂ (An = Th, U) [38] as catalysts precursors (the intermetallic route). These compounds exhibited activity and selectivity for the partial oxidation of methane either for the production of...
synthesis gas [39–41] or for the production of light hydrocarbons [42]. More recently, the study of the catalytic oxidation of methane over acidic KCl-LnCl3 (Ln = La, Ce, Sm, Dy and Yb) molten salts using molecular oxygen as oxidant confirm that the potassium-lanthanide molten salts are active and remarkably selective for the production of C2 hydrocarbons [43].

To our knowledge, the work covering the use of potassium-lanthanide chloride molten salts as catalysts for the activation of methane is scarce and limited to our previous work under oxygen [43]. Here we report, for the first time, the OCM results obtained over potassium-lanthanide chloride molten salt catalysts using N2O instead of O2 as oxidant. All catalysts were characterized by powder X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

All chemicals, KCl and LnCl3 (Ln = La, Ce, Sm, Dy and Yb) were used as supplied (Aldrich). The molten salts components were mixed, ground and pelleted under inert atmosphere (glove box; N2, O2 and H2O < 5 ppm). Unless stated otherwise, all mixtures were prepared with the same eutectic composition (67:33 mol% of KCl and LnCl3, respectively) melted twice under argon at 800 °C (~2 h) and stored in the glove box under air. The XRD patterns were obtained in reflection geometry with a PANalytical X'Pert Pro diffractometer using Cu Kα monochromatic radiation (λ = 1.5406 Å). The operational settings for all scans were voltage = 45 kV; current = 40 mA; 2θ scan range 5°–80° using a step size of 0.03° at a scan speed of 0.02°/min. For identification purposes, the relative intensities (I/I0) and the d-spacing (Å) were compared with standard JCPDS powder diffraction files [46]. A X'PAN800 (KRATOS) spectrometer was used to perform the XPS characterization of the molten salts powders. Measurements were performed with the non-monochromatized Al Kα X-radiation of 1486.6 eV produced using a current of 10 mA and a voltage of 13 kV. Other operating conditions, spectra acquisition details and data treatment are described elsewhere [41,47]. For before reaction (BR) powders, spectra were corrected using as reference the binding energy of CI 2p3/2 = 199.2 eV, typical of CI in KCI or LnCl3 [48]. For after reaction (AR) powders, spectra were corrected using as reference the binding energy of O 1s peak assigned to O–Ln in BR spectrum. For quantification purposes, sensitivity factors were 0.66 for O 1s, 0.25 for C 1s, 0.62 for Cl 2p, 1.24 for K 2p, 6.73 for La 3d5/2, 12.6 for Ce 3d, 18.2 for Sm 3d, 2.75 for Sm 4d, 16.4 for Dy 3d5/2, 3.29 for Dy 4d, 1.01 for Dy 4p1/2, 3.75 for Yb 4d and 1.08 for Yb 4p3/2. The sensitivity factors of the non-lanthanides elements were used as furnished by the equipment library. The lanthanides values were obtained by multiplying the Scofield factors by the equipment response function. This function was obtained as described elsewhere [41].

In order to ensure the maximum contact between the reaction gas and the molten salts, the catalytic oxidation of methane was carried out at atmospheric pressure in two different reactor vessels: a) initially, in a fixed bed quartz reactor where the feed gasses are bubbled through the molten metal’s, as described elsewhere [49] and b) later, in tubular micro-flow quartz type reactor, as described elsewhere [50–52]. The later is also bubbled type reactor with an outer diameter 20 mm, inner diameter 16 mm and column length 210 mm. Preliminary tests proved that the differences between the results obtained in both reactors were insignificant. For practical reasons, the second one was the main reactor used in this work. In both cases, mass flow controllers were used to control CH4 (Air Liquide, purity 99.9999%), N2O (Air Liquide, purity 99.9995%) and He (Air Liquide, purity 99.9995%) flows and a thermocouple was placed on the catalytic bed for continuous monitoring of the sample temperature. Blank tests performed without catalyst revealed that the molten salts weight losses were less than 0.5 wt.%.

Unless otherwise stated, a gaseous mixture of CH4 (3%), N2O (6%) and He (91%) was introduced and the reaction was studied with an adequate Gas Hourly Space Velocity (GHSV) of 1200 mL of CH4/g of catalyst per h (m = 20–100 mg) at 750 °C. The outlet gas was firstly bubbled in water to remove HCl and, secondly, cooled in an ice-water trap prior to analysis. Its composition was analyzed on-line as described elsewhere [39–41]. The confidence level for the reagents and products quantification was better than 95%. Unless otherwise stated, the values reported in this paper represent the catalysts activities at steady state after 1 hour on stream.

3. Results and discussion

3.1. Catalytic behavior

KCl–LnCl3 (Ln = La, Ce, Sm, Dy and Yb) molten salts were active and selective for the activation of methane using nitrous oxide as oxidant (Fig. 1). The activity increases with the temperature (Fig. 1A) and the reaction main products were C2 hydrocarbons (ethane and ethylene) and CO, CO2 (oxidation products represented as COx, data not shown) (Fig. 1B). The formation of H2 and O2 was never detected. Blank tests performed at 750 °C (without catalyst) show also an irrelevant contribution due to the thermal decomposition of N2O or thermal activation of CH4 (e.g. CH4 conversion < 1% and COx selectivity = 100%).

The results obtained at 750 °C represent the best compromise between the desired high conversion of methane and higher production of C2 hydrocarbons. At such temperature, all catalysts are highly selective to C2 hydrocarbons (conversion 10–20%, selectivity 70–80%). At temperatures higher than 750 °C, the reaction kinetics is controlled by...
the thermal activation of both reagents, which explain the dominant formation of oxidation products.

The conversion of methane increases along the lanthanide series when La is substitute by Ce, Sm or Dy (CH4 conversion ≈ 10, ≈ 14 and ≈ 20% for Ln = La, Ce or Sm and Dy, respectively), except for the potassium-ytterbium chloride molten salt, which points for an f-block element influence on the catalysts properties. One possible explanation for the Yb exception can be attributed to the proprieties of such molten salt catalyst that melts only at 771 °C. Therefore, at 750 °C the sample is on the solid state, whereas all the other catalysts are on the molten state. Apparent activation energies (Ea) were calculated using the Arrhenius equation and assuming a first order reaction. The values obtained (147, 143, 136, 118, 132 ± 1.4 kJ/mol for Ln = La, Ce, Sm, Dy and Yb, respectively) are in line with those reported in the literature (≈ 140 kJ/mol) [53] and clearly decrease along the lanthanide series in agreement with the increase of the catalyst activity when La is replaced by Ce, Sm or Dy.

The potassium-lanthanide chloride molten salts were also very stable to deactivation for a long time on the gaseous stream. As a example, the conversion of methane over the lanthanum molten salt catalyst (≈ 11%) was stable for at least 48 h on stream (Fig. 2). The oxidation products (CO2) and C2 hydrocarbons (≈ 20 and ≈ 80%, respectively) selectivities were also remarkably constant and, in particular, the selectivity to hydrocarbons was very high.

On the other hand, if we compare such results with those previously reported by our group, under O2 [43], the molten salt catalysts are less active under N2O (Fig. 3A), but more selective to C2 hydrocarbons (80% versus 80%). Consequently, an oxidant effect exists that is very similar to other previously reported in the literature: the addition of oxygen during the activation of methane with N2O increases the conversion of methane and decreases the selectivity to hydrocarbons [54].

The results reported on Fig. 3 confirm also the effects of the rare earth metal ions oxidation-reduction potential (E) and mobility of rare earth trivalent ions (bo) in molten KCl on the catalyst activity and selectivity to hydrocarbons previously reported under O2 [43,55–57], namely the increase of the production of hydrocarbons with rare earth metal ions oxidation-reduction potential.

Therefore, it can be said that the potassium-lanthanide chloride molten salts are catalytically active for the conversion of methane and highly selective for the production of C2 hydrocarbons using N2O as oxidant. They are also remarkably stable for long periods of time on stream (at least 48 h) and the selectivity to hydrocarbons increases when N2O replaces O2 as oxidant. To our knowledge, this is the first time that such results are reported in the literature using potassium-lanthanide chloride molten salts as catalysts.

**Fig. 2.** Catalytic conversion of CH4 and selectivity to C2 hydrocarbons and CO2 over the KCl-LaCl3 molten salts as a function of time on stream at 750 °C.

**Fig. 3.** Effect of the type of oxidant on the catalytic activation of CH4 over the KCl–LnCl3 molten salts at 750 °C (O2, full symbols; N2O, open symbols; bo, mobility parameter and E (Ln3+ / Ln°), reduction potential of the lanthanide ions in molten KCl[43]).

### 3.2 Catalyst characterization

It is known that most metal chlorides, and among them the alkali chlorides, alkaline earth chlorides, divalent transition metal chlorides and lanthanide chlorides, are typical cases of high temperature ‘ionic’ liquids. The structure of such species has been the subject of numerous investigations. In particular, the study of the AX–LnX3 (A = alkali metal, X = halide, Ln = lanthanide) molten salts high temperature structural spectroscopic work done by George Papatheodorou since the early 70s [58]. It was well established that the structural units present in e.g. KCl–LnCl3 molten mixtures are mainly the LnCl2+ units and not merely Ln3+ ions. For the larger cations (La and Nd) a higher coordination of seven or eight is also possible.

In situ high temperature spectroscopic characterization applied to molten salts is of great importance since it adds fundamental data to the chemistry of molten salts in the liquid phase. However, only a few methods, e.g. NMR and ESR, have been applied to such in situ spectroscopic studies [59]. To our knowledge, in situ real-time spectroscopic characterization of chloride molten salt catalytic active centers under high temperature and reactive catalytic gaseous conditions was never reported.

In this work, all analyses were performed before and after reaction on the solidified melt. Under oxidative conditions and after stopping the reaction and cooling down the reactor, the catalysts composition at the surface suffers important modifications which occur only due to the catalytic reaction leaving also a fingerprint on the solidified melt. XRD analysis before reaction confirms the presence of the K2LnCl3 molten salt phase (Fig. 4). XRD analysis after reaction shows the presence of lanthanide oxides and potassium chloride on the catalysts surface, except for the lanthanum compound where the formation of an oxide phase is replaced by the formation of an oxychloride phase.
the lanthanum compound, see Table 1 below). The formation, under oxidative conditions, of stable oxides and oxychlorides insoluble in the molten salt is known from the literature [60]. The formation of lanthanide oxychlorides in the melt is thermodynamically favorable at low temperatures, but the formation of the oxide phase becomes preponderant at higher temperatures \(T > 650 \, ^\circ\text{C}\), except for CeCl\(_3\). For the cerium chloride system, the formation of CeO\(_2\) is thermodynamically favored at low temperatures \(T > 200 \, ^\circ\text{C}\) [60]. In other words, under oxidative conditions the formation of a layer composed by oxides and oxychloride species turn out to be the dominant phase at the surface after solidification.

However, more work has to be done and more analysis is necessary. Especially for what concerns the extent of the formation of rare earth oxides and oxychlorides with the time of reaction that depends on the formation of oxygen (in this work its only source is N\(_2\)O), its solubility in the molten salt and the diffusion of the oxygen ions \((\text{O}^2-)\) toward the free rare-earth ions \((\text{RE}^{3+})\) that, in our opinion, is away from this work purpose.

Fig. 5 shows the XPS spectra obtained in the O 1s, Cl 2p and C 1s plus K 2p regions of representative catalysts. O 1s is fit with three main components: at 530.4 ± 0.5 eV, 532.2 ± 0.3 eV and 533.4 ± 0.2 eV assigned to oxygen bound to the lanthanide (oxidized O-Ln, e.g. Ln\(_2\)O\(_3\)), lanthanide hydroxides (Ln-\(\text{OH}\)) and organic oxygen (\(\text{O}_{\text{org.}}\), e.g. Ln-\(\text{OC}_{\text{n}}\)\(_{\text{m}}\), respectively [40,48,61]). Before reaction, K-La salt exhibits only the two O 1s peaks assigned to oxidized lanthanum or hydroxide lanthanum, but after reaction an extra peak at higher BE corresponding to organic oxygen appears. A similar behavior can be found for K-Dy and K-Yb salts: a very weak peak assigned to organic oxygen before reaction greatly increases after reaction. In K–Ce and K–Sm, after reaction, O 1s regions are composed by two components with FWHM wider than before reaction (FWHM = 2.4 eV (AR) and 1.9 eV (BR)). Thus the component centered at higher BE can include the contribution of organic oxygen as well.

K 2p and C 1s neighbor regions also suffer important modifications with the catalytic reaction. C 1s region contains one component centered at very low BE (= 283.7 ± 0.5 eV) due to graphitized carbon and, probably, carbon bound to the lanthanide; the other peaks correspond to aliphatic carbons (sp\(^3\) carbons centered at 285.2 ± 0.2 eV), and, probably, carbon bound to the lanthanide; the other peaks correspond to aliphatic carbons (sp\(^3\) carbons centered at 285.2 ± 0.2 eV), carbon bound to oxygen \((\text{C} = \text{O}, \text{C} = \text{O})\) between 286 and 288 eV) and/or, where chlorine is detected, C–Cl (287 eV); in samples

Therefore, the initial K\(_2\)LnCl\(_5\) (\(\text{Ln} = \text{La, Ce, Sm, Dy and Yb}\)) eutectic molten phases at surface are to some extent transformed after reaction into oxides and oxychlorides species, which correlate with the surface content of K and Cl that decrease drastically after reaction (except for K 2p and C 1s neighbor regions also suffer important modifications with the catalytic reaction. C 1s region contains one component centered at very low BE (= 283.7 ± 0.5 eV) due to graphitized carbon and, probably, carbon bound to the lanthanide; the other peaks correspond to aliphatic carbons (sp\(^3\) carbons centered at 285.2 ± 0.2 eV), carbon bound to oxygen \((\text{C} = \text{O}, \text{C} = \text{O})\) between 286 and 288 eV) and/or, where chlorine is detected, C–Cl (287 eV); in samples

### Table 1

**XPS atomic % and atomic ratios before (BR) and after reaction (AR).**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>La–K–Cl</th>
<th>Ce–K–Cl</th>
<th>Sm–K–Cl</th>
<th>Dy–K–Cl</th>
<th>Yb–K–Cl</th>
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<tbody>
<tr>
<td></td>
<td>BR</td>
<td>AR</td>
<td>BR</td>
<td>AR</td>
<td>BR</td>
</tr>
<tr>
<td>At. conc. (X)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K 1s</td>
<td>18.06</td>
<td>23.55</td>
<td>12.27</td>
<td>33.42</td>
<td>14.63</td>
</tr>
<tr>
<td>K 2p</td>
<td>0.04</td>
<td>9.78</td>
<td>22.05</td>
<td>21.74</td>
<td>28.54</td>
</tr>
<tr>
<td>Cl 0</td>
<td>1.37</td>
<td>9.78</td>
<td>22.05</td>
<td>21.74</td>
<td>28.54</td>
</tr>
<tr>
<td>Ce 1s</td>
<td>0.43</td>
<td>6.07</td>
<td>5.90</td>
<td>3.57</td>
<td>6.03</td>
</tr>
<tr>
<td>Sm 1s</td>
<td>0.90</td>
<td>3.52</td>
<td>6.03</td>
<td>3.52</td>
<td>0.94</td>
</tr>
<tr>
<td>Yb 1s</td>
<td>0.33</td>
<td>0.58</td>
<td>0.37</td>
<td>0.50</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Atomic ratios**

<table>
<thead>
<tr>
<th></th>
<th>K/Ln</th>
<th>Cl/Ln</th>
<th>Cl/(K + Ln)</th>
<th>O/(K + C)</th>
<th>(\text{O}<em>{\text{org.}}/\text{O}</em>{\text{total}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K 1s</td>
<td>3.19</td>
<td>1.61</td>
<td>3.74</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>Cl 0</td>
<td>1.1</td>
<td>0.5</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O/(K + C)</td>
<td>0.224</td>
<td>0.153</td>
<td>0.233</td>
<td>0.512</td>
<td>0.338</td>
</tr>
<tr>
<td>(\text{O}<em>{\text{org.}}/\text{O}</em>{\text{total}})</td>
<td>0.33</td>
<td>0.58</td>
<td>0.37</td>
<td>0.50</td>
<td>0.32</td>
</tr>
</tbody>
</table>

\(a\) Not detected or residual.

\(b\) K 2p has a strong intensity, but it is overlapping Dy 4p\(_{\frac{3}{2}}\) (cf. Fig. 5).

\(c\) The Cl 2p tail overlaps La 4p\(_{\frac{3}{2}}\) (cf. Fig. 5).

\(d\) Cl 2p has a strong intensity, but it is overlapping Yb 4d (not shown).

\(e\) Not quantifiable.

\(f\) Overlapping Si 2s in the AR sample (Si 2s has a very weak intensity and is centered at 153 eV; Silicon comes from the double face tape used to fix the sample).

\(g\) \(\text{O}_{\text{org.}}\): organic oxygen and or hydroxides; \(\text{O}_{\text{total}} = \text{O}_{\text{org.}} + (\text{Ln-}\text{OH}) + \text{O-Ln}\) (see text and Fig. 5).
K–Ce (BR) and K–Yb (AR), also carbonate (peak centered at 290.5 ± 0.2 eV) is detected. In K–La before reaction C 1s peak is assigned to graphitized carbon. This carbonaceous overlayer attenuates the XPS signal of other elements, namely chlorine, potassium and lanthanum. The same is observed for K–Ce, K–Sm, K–Dy and K–Yb.

Table 1 shows the XPS relative atomic concentrations of oxygen, chlorine, potassium and lanthanides and some relevant atomic ratios for all salts analyzed before and after reaction. The quantitative analysis shows that the eutectic molten phase, K2LnCl5, present in bulk, is also at the surface, but in some salts this is not the only phase. Before reaction, the ratio Cl/(K + 3 * Ln) should be 1 for the eutectic phase. This was found for La (1.1 ± 0.1), Sm (0.9 ± 0.1) and, approximately, for Dy salts (1.2 ± 0.1), whereas Cl/(K + 3 * Ln) < 1 (0.7 ± 0.1), found for Ce and Yb salts, suggest the presence of surface “impurities”; namely, lanthanide oxides and/or hydroxides that increase after reaction. The quantitative analysis shows also that the oxygen surface concentration largely increases after reaction increasing the O/(Ln + C) ratio, meaning that the lanthanide chlorides become oxides or oxychlorides during reaction.

After reaction, the atomic ratios Cl/(K + 3 * Ln), Cl/Ln and K/Ln decrease in all salts. Potassium and chlorine content are lower or not detected after reaction in all the samples, which supports the formation of lanthanide oxides and/or hydroxides at the catalysts surface during reaction. However, the low content of potassium and chlorine detected is most probably related to the huge amount of graphitized carbon present at the catalysts surface. This is in agreement with the XRD measurements which show only small amounts of KCl (Fig. 4).

Therefore, it can be said that the analysis of the catalysts by XRD and XPS before and after reaction reveals important modifications on the solidified melt surface. Namely, after reaction and in addition to the metallic O²⁻ oxygen (O–Ln) present in all the systems, the surface seems to be enriched with other oxidized species (Ln – OH and organic C – O, C=O, O – C – O or C – OH are also among these other oxidized species) that could be linked to the catalysts behavior and time on stream, see Fig. 5 and Table 1.

It is generally accepted that in catalysis: i) the active sites type, amount and accessibility are the main factors that govern the catalyst activity and selectivity [62–64] and ii) that the reactions of methane
conduct by formation of gaseous methyl radicals from the interaction of the methane with either adsorbed or lattice catalysts oxygen. The reaction studied in this work requires catalytic active sites for both NO and CH₄ (formation of anion radical oxygen species and methyl radicals) through and oxidation–reduction cycle [65]. For the activation of methane with nitrous oxide, the first step occurring is the formation of active oxygen species upon NO₂ decomposition over the catalyst surface [5,66,67]. They participate in selective (olefin production) and non-selective (CO₂ formation) heterogeneous reactions. The generated surface species are very important for the activation of low alkanes. In the case of CH₄, methyl radicals are formed primarily on the catalyst surface, followed by desorption and coupling to ethane. The ethylene is obtained by dehydrogenation of ethane [18].

In this work, we have found that the increase of oxygen, including hydroxide and chloride surface species after reaction on the solidified melt seems to correlate with a beneficial effect on the catalysts activity in detriment of the selectivity to hydrocarbons. Good correlations were obtained between atomic ratios of the total number of chloride, oxygen (including hydroxides, data not shown) and lanthanide species determined by XPS and the evolution of the catalysts activity and selectivity either using N₂O or O₂ as oxidant (Fig. 6). The increase of the number of surface oxygen species, including hydroxides, increases the catalysts activity, whereas the overall selectivity to hydrocarbons decreases with it.

Miller et al. [68] studied the selective catalytic reduction of NO₂ over cobalt zeolite catalysts and established a direct correlation between the increase of the number of acid sites and the catalysts activity for the decomposition of NO₂. Miller found an inverse correlation between the catalyst surface basicity (measured by the catalysts number of hydroxide species) and the selectivity to hydrocarbons (lower number of hydroxide species implies higher selectivity and decrease on catalysts oxidant strength). The importance of OH species on the selective catalytic reduction (SCR) of NO₂ by CH₄ in the absence of O₂ was also mentioned before for catalytic behavior of Fe on a BEA Zeolite [69]. Our results emphasize Miller conclusions and the decrease of the overall selectivity to hydrocarbons can be explained by the increase of surface oxygen species, namely hydroxides (the presence and stability of surface hydroxides at high temperatures (>700 °C) are known facts from the literature [62–64], which are directly linked to the formation of oxidation products).

On the other hand, higher activity is observed for the catalysts which have the higher amount of surface chloride species before reaction, in detriment of the selectivity to hydrocarbons. Nevertheless, further work is required in order to determine the real active species in the molten salts, namely the catalytic behavior of the LnCl₆⁻ units.

4. Conclusions

The activation of methane was studied over potassium-lanthanide chloride molten salt catalysts using NO₂ as oxidant and the main products were hydrocarbons. The best results were those obtained at 750 °C over the lanthanum, cerium and samarium molten salts (selectivity > 75%). The factors that seem to contribute to the variation of the activity and selectivity along the lanthanide series are the acidic properties of the catalysts and the oxidative character of the rare earth trivalent ions in the potassium chloride molten melt. To our knowledge, this is the first time that such results are reported over rare earth chloride molten salts, which could lead to an entirely new direction for molten salts applications using them as catalysts.

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References


Fig. 6. Oxygen and chlorine species after reaction content effect on the catalysts activity and selectivity to hydrocarbons (N₂O, black symbol; O₂, gray symbol fill).