ABSTRACT: Commercialization of CH₄ valorization processes is currently hampered by the lack of suitable catalysts, which should be active, selective, and stable. CH₄ oxychlorination is one of the promising routes to directly functionalize CH₃Cl and lanthanide-based catalysts show great potential for this reaction, although relatively little is known about their functioning. In this work, a set of lanthanide oxychlorides (i.e., LnOCl with Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) and Er- and Yb-based catalysts were synthesized, characterized, and tested. All lanthanide-based catalysts can directly activate CH₄ into chloromethanes, but their catalytic properties differ significantly. EuOCl shows the most promising catalytic activity and selectivity, as very high conversion levels (>30%) and chloromethane selectivity values (>50%) can be reached at moderate reaction temperatures (∼425 °C). Operando Raman spectroscopy revealed that the chlorination of the EuOCl catalyst surface is rate-limiting; hence, increasing the HCl concentration improves the catalytic performance. The CO selectivity could be suppressed from 30 to 15%, while the CH₄ conversion more than doubled from 11 to 24%, solely by increasing the HCl concentration from 10 to 60% at 450 °C. Even though more catalysts reported in this study and in the literature show a negative correlation between the S_CO and HCl concentration, this effect was never as substantial as observed for EuOCl. EuOCl has promising properties to bring the oxychlorination one step closer to an economically viable CH₄ valorization process.

KEYWORDS: lanthanide, methane, oxychlorination, reaction mechanism, operando spectroscopy

1. INTRODUCTION

The use of CH₄ from natural gas in chemical industry is expected to grow in the coming years, especially in view of the lower CO₂ footprint relative to other fossil-based resources, such as coal and crude oil.¹ CH₄ is used in the synthesis of chemical building blocks, such as ammonia, methanol, and acetic acid.²⁵ Central in the synthesis of these molecules is the partial oxidation of methane to CO and H₂ via reforming reactions, followed by one or more synthesis steps to obtain the desired reaction product.³ A major drawback of this approach is the energy-intensive, multistep process to obtain the desired bulk chemicals. Direct conversion routes of CH₄ into chemical building blocks could reduce the energy needed for CH₄ upgrading. To this date, however, direct conversion routes have not been commercialized because high selectivity is often only achieved at low conversion levels, while high conversion levels lead to the formation of, for example, CO₂.²⁵

The direct conversion of CH₄ into halogenated CH₄, such as CH₂Cl₂ and CH₃Br, via, for example, methane oxychlorination (MOC)⁶⁻¹¹ and methane oxybromination,⁶¹²⁻¹⁵ is a promising route for efficient hydrocarbon utilization.¹⁶ Compared to other direct conversion routes of CH₄, high selectivity to the desired product and relatively high conversions can be achieved, while being operated under moderate reaction conditions (i.e., in the 400–600 °C temperature range and with p = ∼1 bar).¹⁴ Chlorinated methanes (CMs) are commodity chemicals, and CH₃Cl is especially of great interest due to the chemical analogy between CH₃Cl and CH₃OH.⁹,¹⁷ It can serve as a building block for the production of added value commodity chemicals, such as ethylene, propylene, and acetic acid.³¹⁸ Therefore, a high selectivity to the desired CH₃Cl is of great interest in the open literature⁵⁻¹¹,¹⁴,¹⁹⁻²⁵ and in the patent literature. However, the selective conversion of CH₄ into CH₃Cl remains challenging. The polarized bonds in the functionalized molecule are often more reactive than the inert C–H bonds present in CH₄ resulting in undesired byproduct formation.⁵,⁶ For MOC, other chlorinated products, such as CH₂Cl₂, are thus also obtained. In the upgrading of CH₃Cl into olefins, even small amounts of CH₂Cl₂ cause rapid zeolite deactivation and thus
CHCl₃ needs to be removed from the feedstock. This increases the cost to separate CH₂Cl and requires the development of, for instance, the hydrodechlorination process to convert poly-chlorinated CH₄ into CH₂Cl₂.

Olah et al. found that inserting an electrophilic Cl atom catalytically over solid (super)acids could reverse CH₄ over-functionalization and obtain high yields toward CH₂Cl₂ for direct chlorination. However, the chlorination of CH₄ via the oxychlorination reaction is preferred because it utilizes HCl, produced as a byproduct in chlorination reactions, with a 100% Cl atom efficiency. In comparison, the Cl atom efficiency of thermal chlorination reactions is only 50%. This concept of an electrophilic Cl atom was successfully adapted by Podkolzin, Lercher, and co-workers and applied in the MOC reaction over LaOCl. Interestingly, a reaction mechanism was proposed where La³⁺ catalyzes the reaction without changing the oxidation state. The activation of terminal surface lattice Cl by the dissociative adsorption of O₂ results in a surface hypochlorite (ClO⁻), where the formal oxidation state of chlorine changes from −1 to +1. CH₄ coordinates to this hypochlorite, and an atom exchange occurs, leaving a hydroxyl group on the surface and the CM. This surface hydroxyl group reacts with HCl to regenerate the chlorinated surface, producing water. Bulk LaOCl catalysts with a S BET of around 20 m²/g were activated with HCl and were able to chlorinate CH₄. At moderate conversion levels (X CH₄ = 10%), S₂CH₂Cl~80% was obtained with minor byproducts of CH₂Cl₂ (12%) and CO (8%), essentially free of CO₂, CHCl₃, and CCl₄.

However, the selectivity was only obtained at low conversion levels (X CH₄ = <10%). As the conversion of CH₄ was increased (X CH₄ = ~18%), the CO yield would surpass the CH₂Cl₂ yield. Overoxidation of CH₄ into CO₂ at high conversion levels is the biggest challenge in the catalyst and process development for the MOC reaction. Controlling the degree of surface chlorination of the solid catalysts, while maintaining a high conversion level is crucial for an economically viable process. For lanthanum-based catalysts, it is known that the CH₄ chlorination step leaves a terminal surface lattice oxygen, while the exact same site is also responsible for the catalytic destruction of polychlorinated hydrocarbons. Balancing the chlorination rate with HCl and dechlorination rate by the reaction with CH₄ and O₂ is crucial for controlling the catalyst selectivity.

While a handful of publications report on the use of lanthanum, cerium, and europium oxychlorides, the rest of the lanthanide series remains so far largely unexplored. Lanthanides are interesting due to their high stability in corrosive environments and tunable redox properties and are thought to exhibit comparable chemistry in the oxychlorination reaction. Europium-based catalysts were previously reported as promising ethylene/propylene oxychlorination and CH₄ oxybromination catalysts. The well-tailored redox properties of EuOX (with X = Cl or Br) were crucial in developing active and selective catalysts. Less successful was the use of EuOCl in MOC, where overoxidation seemed to be a large issue. For instance, a S CO value of ∼20% was observed at similar CH₄ conversion levels, which is too high for industrial application.

In this work, we have performed a comprehensive study on the CH₄ oxychlorination over a series of lanthanide-based catalysts with the general formula LnOCl, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. Two other lanthanide catalysts, Er- and Yb-based, were also synthesized with the same synthesis technique, which did not yield the LnOCl phase. Although not all lanthanide-based catalysts showed equally high activity, this study revealed that they can be used to directly activate CH₄ into CMs. Moreover, we show that a EuOCl catalyst possesses unique characteristics that make it possible to develop catalysts with high conversions and low selectivity toward CO₂ as unwanted byproducts. Central in this study is the possibility to operate a EuOCl catalyst in HCl-rich environments. The CO selectivity could be suppressed, while the CH₄ conversion more than doubled, solely by increasing the HCl concentration. Even though more reported catalysts show this behavior (e.g., CeO₂ when HCl % 6% → 15%, X CH₄, ~31% → ~34% and S CO ~17% → ~15%), this effect was never as substantial as observed for EuOCl. Furthermore, new mechanistic insights into the working principles of this superior EuOCl catalyst material were obtained by using operando spectroscopy.

2. EXPERIMENTAL METHODS

2.1. Catalyst Synthesis. LnOCl (where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) and Er- and Yb-based catalyst materials under study were prepared by dissolving the corresponding lanthanide(III) chloride salt (LnCl₃·xH₂O, Fisher Scientific, >99%) in ethanol (absolute, VWR), followed by a precipitation using stoichiometric amounts of ammonium hydroxide (Fisher Scientific, 25% in H₂O) at room temperature. After the dropwise addition, the precipitates were stirred for an additional hour and subsequently centrifuged to obtain the gel.

Then, the obtained gel was washed with ethanol (absolute, VWR) and dried at 80 °C. Lastly, the dried solids were calcined in a static oven at 500 °C for 3 h using a ramp rate of 5 °C/min.

2.2. Catalyst Characterization. X-ray diffraction (XRD) patterns were obtained with a Bruker-AXS D2 Phaser powder X-ray diffractometer in Bragg–Brentano geometry, using Co Kα1,λ = 1.79026 Å, operated at 30 kV. The measurements were carried out between 10 and 80° with a step size of 0.05° and a scan speed of 1 s, with a 2 mm slit for the source. N₂ adsorption isotherms were measured at 77 K on a Micromeritics TriStar II Plus instrument. Prior to all measurements, samples were dried at 573 K under a flow of N₂. Specific surface areas were calculated using the multipoint BET method (0.05 < p/p₀ < 0.25). Pore volumes were calculated by the t-plot method; pore size distributions were obtained by BJH analysis. Transmission electron microscopy (TEM) was performed on a FEI Tecnai 20 instrument operating at 200 kV.

Operando spectroscopy measurements were performed with an AvaRaman-S32 HERO-EVO instrument (λ = 532 nm, laser output 50 mW, spectral resolution of 10 cm⁻¹) equipped with an AvaRaman-PRB–FC–S32 probe, capable of withstanding temperatures up to 500 °C. Spectra were collected every minute with the AvaSoft 8 software. The data were subsequently baseline corrected and normalized. The initial Raman intensity was optimized to obtain at least 50% of the saturation value. The operando Raman experiments were performed by a sequential chlorination, dechlorination and oxychlorination step. The chlorination reaction was performed at 450 °C with a HCl/N₂ ratio of 20:20 (mL/min) for 2 h. Subsequently, the reactor was heated to 500 °C under N₂, and then, flows CH₄/HCl/O₂/N₂/He of 2:0:1:1:1:16 and CH₂Cl₂/HCl/O₂/N₂/He of 2:2:1:1:14 were applied for dechlorination (90 min) and oxychlorination (2 h), respectively. The operando photoluminescence spectroscopy...
experiments were performed by two sequential ramp experiments from 450 to 520 °C at 1 °C/min under the CH₄/HCl/O₂/N₂/He ratio of 2:2:1:1:14. Prior to the first ramp experiment, the catalyst was subjected to the ratio CH₄/HCl/O₂/N₂/He of 2:2:1:1:14 for 2 h at 450 °C. Prior to the second ramp experiment, the catalyst was subjected to a CH₄/HCl/O₂/N₂/He ratio of 0:4:0:1:14.

2.3. Catalyst Testing. All the catalytic tests and operando Raman measurements were performed in a lab-scale continuous-flow fixed-bed quartz reactor. Details of the setup, including a schematic and some pictures, are shown in Figure S1.

In a typical experiment, 500 mg of the catalyst material (with a 125–425 μm size fraction) was loaded in a quartz reactor and heated to 450 °C under N₂ with 10 °C/min. The catalyst was activated in 20% HCl/N₂ for 2 h prior to catalysis. For the isothermal experiments, the temperature was adjusted to reach X_C₄H₄ = 10% for the CH₄/HCl/O₂/N₂/He ratio of 2:2:1:1:14. When stable conversion was reached, the HCl/He ratio was adjusted, so that the HCl concentration was increased to 20, 40, 60, and 80%, while keeping a constant flow of 20 mL/min. For the ramp experiments, the reactor was brought to 350 °C and the desired feed mixture (i.e., CH₄/HCl/O₂/N₂/He of 2:2:1:1:14 or 2:16:1:1:0 in mL/min) was fed into the reactor. A stabilization period of 30 min was applied, and then, the ramp experiment of 1 °C/min was commenced at 550 °C. For the stability test, the temperature of the reactor was brought to 450 °C under N₂. After a stabilization period of 15 min, the flow was adjusted to the CH₄/HCl/O₂/N₂/He ratio of 2:2:1:1:14 (in mL/min) and carried out for 10 h. Subsequently, the HCl/He ratio was adjusted, so that the HCl concentration was increased to 20, 40, 60%, and finally 80% HCl, while keeping a constant flow of 20 mL/min. Every feed ratio was tested for 10 h, except for 80% HCl, which was tested for 8 h. During the stability test, operando Raman spectroscopy measurements were performed.

The CH₄ conversion, X_C₄H₄, and O₂ conversion, X_O₂, are calculated according to eq 1

\[ X_i(\%) = \frac{x_{\text{inlet}} - x_{\text{outlet}}}{x_{\text{inlet}}} \times 100\% \times \text{ISCF} \]

where x_{\text{inlet}}, x_{\text{outlet}} and ISCF stand for the volumetric concentration of compound a at the inlet and outlet of the reactor and the internal standard correction factor, respectively. The yield of product i, Y_i, is calculated according to eq 2

\[ Y_i(\%) = \frac{x_i}{x_{\text{CH}_4,\text{inlet}}} \times 100\% \times \text{ISCF} \]

where x_i and ISCF stand for the volumetric concentration of carbon-containing product i and the internal standard correction factor, respectively. The selectivity of product i, S_i, is calculated according to eq 3

\[ S_i(\%) = \frac{Y_i}{X_{\text{CH}_4}} \times 100\% \]

The CH₄ reaction rate is calculated according to eq 4

\[ R_{\text{CH}_4}(\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}) = \frac{P \times F_T \times x_{\text{CH}_4,\text{inlet}} \times X_{\text{CH}_4}}{R \times T \times W_{\text{cat}}} \]

where P, F_T, R, T, and W_{\text{cat}} stand for the pressure, total flow, gas constant, ambient temperature, and catalyst weight. Finally, the carbon balance was calculated and measurements with their carbon balance >± 5% were removed. The carbon balance was calculated according to eq 5.

\[ \text{Carbon balance} = \sum Y(i) + 100 - X_{\text{CH}_4} \] (5)

3. RESULTS AND DISCUSSION

3.1. Catalyst Properties. All synthesized lanthanide oxychloride (LnOCl) materials, made by precipitating LnCl₃·xH₂O with ammonium hydroxide, were characterized in detail with a battery of analytical methods. The result is a set of solid catalysts with surface areas, crystal phase, and particle morphology in the same order of magnitude. This enables us to study the role of the lanthanide ion within the LnOCl structure and its effect on MOC performances. As an example, Figure 1 shows the XRD patterns of the as-synthesized catalysts.

![Figure 1](https://doi.org/10.1021/acscatal.1c00393)
and HoO\textsubscript{2}Cl\textsuperscript{35} were observed in the case of HoOCl, but the dominating phase is LnOCl. Unfortunately, for Er and Yb, we were not able to obtain a similar crystal phase, as indicated by the absence of the typical XRD peaks observed for the other LnOCl. In addition, the broadness of the XRD peaks suggests relatively small crystalline domains. For simplicity, we have labeled the Er and Yb catalyst as ErOCl and YbOCl, respectively, although this is formally incorrect.

An overview of the physicochemical properties of the as-synthesized catalysts is given in Table S1. The BET surface area \(S_{\text{BET}}\) within the same order is obtained, albeit we noted some variations, ranging from 15.5 m\textsuperscript{2}/g (YbOCl) to 50.2 m\textsuperscript{2}/g (SmOCl). Similarly, the determined pore volume \(V_{\text{pore}}\) ranges from 0.05 cm\textsuperscript{3}/g (PrOCl) to 0.23 cm\textsuperscript{3}/g (EuOCl). All the other \(S_{\text{BET}}\) and \(V_{\text{pore}}\) values fall within this range and correspond well to the \(S_{\text{BET}}\) reported for the same synthesis of LaOCl materials by a base precipitation method.\textsuperscript{10,17,21,22}

As the catalysts are bulk materials and made with base precipitation, ill-defined particles with a particle size ranging from a few nanometers to hundreds of nanometers are obtained (Figures 2 and S2). Especially for the YbOCl material, smaller particles were absent and only larger irregularly shaped particles were observed (Figure S2).

The fact that the \(S_{\text{BET}}\) values (Table S1) are in the same range (15.5–50.2 m\textsuperscript{2}/g) and that the catalyst materials are synthesized in the same crystal structure, allows us to fairly compare the set of synthesized catalyst materials and study the unique role of the lanthanide element on the activity and selectivity observed in the reaction. HoOCl, ErOCl, and YbOCl do not fully comply with these criteria, but because interesting catalytic behavior was observed, and a complete overview of the lanthanide series could be presented, these catalyst materials are also included in this study.

### 3.2. Catalytic Performances

The catalytic activity of the as-synthesized lanthanide-based catalyst materials was compared by performing temperature ramp experiments under standard oxychlorination conditions for the production of CH\textsubscript{3}Cl. \(X_{\text{CH}_4}\), and selectivity are plotted versus the temperature in Figure 3 for every catalysts individually. The selectivity is plotted when both CH\textsubscript{3}Cl and CO were above the detection limit of the GC and the onset temperature at which the catalyst become active is determined as the temperature at which \(X_{\text{CH}_4} > 2\%\).

All catalysts tested in this study show activity in the MOC reaction. Furthermore, the catalyst materials follow the same trend that \(X_{\text{CH}_4}\), \(S_{\text{CO}}\), and \(S_{\text{CH}_2\text{Cl}_2}\) increase with the increasing temperature, while \(S_{\text{CH}_3\text{Cl}}\) decreases. Nevertheless, unique catalytic behavior can be observed when comparing the catalyst materials, and large differences in activity and selectivity were observed.

LaOCl, known for its high \(S_{\text{CH}_4}\),\textsuperscript{10,22} becomes active at 480 °C and reaches a maximum \(X_{\text{CH}_4}\) of 21% at 550 °C. With the increasing temperature, \(S_{\text{CH}_3\text{Cl}}\) decreases from 66 to 32% and \(S_{\text{CO}}\) increases from 25 to 45%. Substantial amounts of CH\textsubscript{2}Cl\textsubscript{2} are formed at 550 °C (\(S_{\text{CH}_2\text{Cl}_2} = 18\%\)), while neither CCl\textsubscript{4} nor CO\textsubscript{2} was detected.

PrOCl also becomes active at 480 °C and reaches a maximum \(X_{\text{CH}_4}\) of 20%. However, the selectivity differs drastically compared to the selectivity obtained with LaOCl. Much of CH\textsubscript{4} is converted to CO, which is the dominant product at temperatures >495 °C. All four CMs can be observed at temperatures >535 °C, albeit in very low concentrations in the case of CCl\textsubscript{4} (\(S_{\text{CCl}_4} < 2\%\)).

For NdOCl, the same onset temperature as for LaOCl and PrOCl was found, namely, 480 °C. However, \(X_{\text{CH}_4}\) shows a sharp increase in activity from 495 °C to 520 °C (\(X_{\text{CH}_4} = 5% \to 16\%\)) after which the activity plateaus till 535 °C. During this sharp increase of \(X_{\text{CH}_4}\), the selectivity is also impacted quite drastically as \(S_{\text{CH}_3\text{Cl}}\) decreases from 64 to 38% and \(S_{\text{CO}}\) is increased from 24 to 38%. Subsequently, \(X_{\text{CH}_4}\) increases further and reaches a maximum \(X_{\text{CH}_4}\) of 22%. \(S_{\text{CH}_3\text{Cl}}\) decreases further to 28%, while \(S_{\text{CO}}\) increases to 46%. \(S_{\text{CH}_2\text{Cl}_2}\) increases gradually from 10 to 19%, while CHCl\textsubscript{3} was only detected in minor amounts (\(S_{\text{CH}_2\text{Cl}_2} < 6\%\)).

SmOCl shows higher activity at lower temperatures, as \(X_{\text{CH}_4} > 2\%\) is reached at 465 °C. A gradual increase in the activity is observed up to 550 °C, where it reaches a final \(X_{\text{CH}_4}\) of 16%. \(S_{\text{CH}_3\text{Cl}}\) decreases from 61 to 30%, while \(S_{\text{CO}}\) increases from 28 to 46%. \(S_{\text{CH}_3\text{Cl}}\) increases with the same trend as \(S_{\text{CO}}\) from 11 to 20%. CHCl\textsubscript{3} was detected in minor amounts (\(S_{\text{CH}_2\text{Cl}_2} < 3\%\)).

The catalytic behavior of EuOCl is unique in a number of aspects. EuOCl shows activity already at low temperatures, as \(X_{\text{CH}_4} > 2\%\) is reached at 385 °C. A maximum \(X_{\text{CH}_4}\) of 26% is reached at 485 °C, after which \(X_{\text{CH}_4}\) drops to 19% at 500 °C. Once the temperature further increases, \(X_{\text{CH}_4}\) steadily increases to the maximum \(X_{\text{CH}_4}\) of 38%, which is the highest value for all lanthanide-based catalysts tested here under standard oxychlorination conditions. The nature of this drop in \(X_{\text{CH}_4}\) is discussed in Section 3.4. The unique performance is also reflected in the selectivity plot, where EuOCl has a maximum \(S_{\text{CH}_3\text{Cl}}\) of 75%, which gradually decreases to 29% with the increasing temperature. Both \(S_{\text{CO}}\) and \(S_{\text{CH}_3\text{Cl}}\) increase with the same rate with the increasing temperature, up till the onset of the activity drop at 485 °C. \(S_{\text{CO}}\) further increases, while \(S_{\text{CH}_3\text{Cl}}\) decreases simultaneously up till the end of the drop at 505 °C. From 505 to 550 °C \(S_{\text{CO}}\) plateaus at 42%, while \(S_{\text{CH}_2\text{Cl}_2}\) slightly increases to 24%. CHCl\textsubscript{3}, CCl\textsubscript{4}, and CO\textsubscript{2} were all detected, albeit in very low amounts (\(S_{\text{CH}_2\text{Cl}_2} < 5\%\), \(S_{\text{CCl}_4} < 1\%\), and \(S_{\text{CO}_2} < 2\%\)).

GdOCl, TbOCl, DyOCl, HoOCl, and ErOCl qualitatively show the same trends in activity and selectivity. These catalysts become active at temperatures between 420 and 430 °C, after which \(X_{\text{CH}_4}\) increases very gradually up to 500 °C. Finally, the
$X_{\text{CH}_4}$ increase slightly levels off and reaches the maximum $X_{\text{CH}_4}$ at 550 °C. For GdOCl, TbOCl, DyOCl, HoOCl, and ErOCl, the maximum $X_{\text{CH}_4}$ is 23, 30, 26, 22, and 19%, respectively. Furthermore, these catalysts show similar selectivity profiles. $S_{\text{CH}_3\text{Cl}}$ steadily decreases over the tested temperature range, with the best performance for ErOCl ($S_{\text{CH}_3\text{Cl}}$ 76% → 40%) and the worst performance for DyOCl ($S_{\text{CH}_3\text{Cl}}$ 55% → 16%). $S_{\text{CO}}$ first sharply increases up till ~440 °C and then gradually increases to an $S_{\text{CO}}$ of 51–62% with the best performance again for ErOCl. $S_{\text{CH}_2\text{Cl}_2}$ increases up till ~500 °C after which it levels off/slightly decreases and reaches a final $S_{\text{CH}_2\text{Cl}_2}$ of 10–20%. CHCl$_3$ was only detected in reasonable amounts for TbOCl and did not increase above 6% over the tested temperature range. CCl$_4$ and CO$_2$ were not detected.

Lastly, YbOCl shows relatively low overall activity, as $X_{\text{CH}_4}$ > 2% is reached at 465 °C and reaches a maximum $X_{\text{CH}_4}$ of 11%. $S_{\text{CH}_2\text{Cl}_2}$ decreases from 72 to 56%, and $S_{\text{CO}}$ increases from 16 to 26%. Furthermore, only CH$_2$Cl$_2$ is detected, which grows from

Figure 3. $X_{\text{CH}_4}$ and corresponding selectivity plotted vs the temperature for LnOCl where Ln = (A) La, (B) Pr, (C) Nd, (D) Sm, (E) Eu, (F) Gd, (G) Tb, (H) Dy, (I) Ho, (J) Er, and (K) Yb. Conditions: CH$_4$/HCl/O$_2$/N$_2$/He of 2:2:1:1:14 (in mL/min) from 350 to 550 °C with a ramp rate of 1 °C/min. Selectivity is given when CH$_3$Cl and CO were above the detection limit of the GC.
12 to 18%. No higher CMs were observed, and no CO₂ was detected.

The CH₄ conversion rate and the corresponding selectivity for every catalyst material tested in this study at a temperature of 480 °C are plotted in Figure 4. This comparative plot clearly shows that, even though the catalysts are chemically and physically comparable, large differences in both the activity and selectivity are induced by the lanthanide element. The highest CH₄ conversion rate of 2.43 mmol CH₄ g⁻¹ cat was observed for EuOCl, which is ~13X times higher than that for LaOCl. Based on the CH₄ conversion rate, the following activity ranking was found: Eu > Tb > Gd > Ho > Er > Dy > Sm > Pr ≈ Nd ≈ La > Yb with a maximum X(CH₄) of 24% for EuOCl and a minimum X(CH₄) of 2% for LaOCl (Figure 4). A similar ranking can be constructed based on S(CHCl) (Eu > Pr > Sm > Er > Gd > Ho > Tb > Dy) and S(CHCl₂) + S(CHCl₃) (Eu > Pr > Sm > Er > Gd > Ho > Tb > Dy) at 480 °C. La, Nd, and Yb are not considered with the selectivity ranking, as the CO yield was below the detection limit.

Based on the activity and selectivity performance, EuOCl shows the most promising catalytic behavior, as the highest X(CH₄) and the best selectivity at reasonable conversion levels are found. Interestingly, LaOCl is often reported for its high S(CHCl) at reasonable conversion levels, but compared to the other lanthanide catalysts tested, its catalytic performance is mediocre under the reaction conditions applied here.¹⁰,¹¹,²²

The CH₄ conversion rate and the corresponding selectivity for every catalyst material tested in this study at a temperature of 480 °C are plotted in Figure 4. This comparative plot clearly shows the most promising catalytic behavior, as the highest level.

Based on the abovementioned experimental findings, it is important to better understand the parameters that tune the reaction selectivity. Four key processes occurring during the MOC reaction for LnOCl materials are schematically depicted in Figure 5. These four processes, namely, the oxychlorination of C₁ (arrows 1–4),²¹ a possible pathway for the catalytic destruction of C₂Cl₂ (arrows 5–8),³³,³⁶ chlorination of terminal lattice oxygen (arrow 9), and bulk diffusion of O/Cl (arrow 10), are connected, as they transition over the same surface compositions. The premise is to skip the catalytic destruction cycle and accelerate the oxychlorination cycle. In the catalytic chlorination of methane, surface chlorination via HCl plays a crucial role. Surface hydroxyl groups react with HCl to form surface chlorine and H₂O (arrows 1–2). The surface hydroxyl groups regenerated as C₁ and O₂ react over the surface chlorine (arrows 3–4). However, the oxychlorination cycle can be skipped, once terminal lattice oxygen is formed via condensation via the hydrolysis of surface hydroxyl groups (arrow 5).³⁷ The catalytic destruction of CMs over terminal lattice oxygen of La is well described,³⁸ and it is hypothesized that a similar mechanism plays a role for the lanthanide-based catalysts tested in this study. When the CM catalytically destructs (arrows 6–7), surface chlorination is again obtained, where it crosses paths with the oxychlorination cycle again. H₂O formed during the oxychlorination reaction and surface condensation can react with the formed surface chlorine, regenerating the surface hydroxyl groups (arrow 8). Important note is that terminal lattice oxygen, over which catalytic destruction of CMs can occur, can either be chlorinated with HCl (arrow 9) or exchanged with mobile bulk chlorine (arrow 10). In the case of nonsteady state behavior of the catalyst composition, bulk diffusion of ions is partly accountable for changing catalyst surface compositions.³⁸ Pivotal in the envisaged reaction cycles is the regeneration of the surface chlorine on which MOC can occur and the catalytic destruction of CMs is prevented.

A direct way to influence the degree of surface chlorination is by altering the HCl concentration under isothermal conditions. To investigate this effect, the catalysts were brought to X(CH₄) ≈ 10% and the concentration of HCl in the feed was increased. X(CH₄), S(CHCl), S(CHCl₂), and S(CHCl₃) are shown in Figure 6, while S(CH₂Cl), and S(CC₂) can be found in Figure S3. Generally, four types of responses can be identified for the different catalyst materials tested on the basis of their measured X(CH₄) values: (1) increased activity (Figure 6, first row), (2) steady activity (Figure 6, second row), (3) slowly decaying activity (Figure 6, third row), and (4) instantaneous deactivation (Figure 6, bottom row).

We ascribe EuOCl to the first category; increased activity with the increasing HCl concentration. X(CH₄) is increased from 11 to 25% going from 10 to 60% HCl in the gas feed. Thereafter, the activity seems to plateau up to 80% HCl. The increase in HCl concentration does not only boost the activity but also suppresses S(CC₂) from 28 to 14%. Furthermore, S(CH₂Cl₂) decreases slightly, while S(CH₂Cl₃) and S(CHCl₃) increase with the increasing HCl concentration. The formation of CO is largely caused by the catalytic destruction of CH₂Cl₂ and CH₂Cl₃ by S(CC₂) and S(CH₂Cl₂) / S(CHCl₃) are negatively correlated. The prevention of the catalytic
destruction of higher CMs is evidenced by the observed $S_{CCl4}$ for EuOCl. The increase in HCl concentration thus has a double-sided effect: (1) less surface oxygen where higher CMs can be catalytically destructed on and (2) the generation of more active sites where chlorination of C1 can occur. Carefully choosing the CH4/HCl/O2 ratio is thus of great importance for optimal catalytic activity.

SmOCl, DyOCl, and YbOCl show similar activity response with the increasing HCl concentration, although the exact values differ significantly. Their $X_{CH4}$ is rather insensitive to the HCl concentration in the feed and only increases slightly. $S_{CH3Cl}$ and $S_{CO}$ slightly decrease or remain constant, which is in line with $X_{CH4}$. $S_{CHCl3}$ seems inversely proportional to $S_{CO}$ and $S_{CH3Cl}$ for DyOCl and YbOCl because it shows an upward trend with the increasing HCl concentration (Figure S3A). For SmOCl, no formation of CH3Cl was observed, indicating that no CH3Cl was formed or that all formed CHCl3 was destructed. For these catalyst materials, $S_{CO}$ could not be suppressed as dramatically as for EuOCl (for DyOCl 49% → 37% vs for EuOCl 29% → 14%). A higher degree of surface chlorination mainly results in preventing the catalytic destruction of higher CMs for DyOCl and YbOCl, and to a lesser extent, the generation of more active sites for all three catalysts. The generation of more active sites did not result in a higher $X_{CH4}$ but in a higher overall degree of chlorination of methane. The reactivity of C1 increases with the increasing chlorine content, and it appears that CH4 and the other CMs are in competition over the same active site(s).

LaOCl, GdOCl, TbOCl, HoOCl, and ErOCl all show a decaying activity profile with the increasing HCl concentration in the feed. The activity drops the most for TbOCl ($X_{CH4}$ 12% → 4%) and the least for LaOCl ($X_{CH4}$ 10% → 7%). When further comparing these five catalysts based on their selectivity, LaOCl and ErOCl show very similar behavior and GdOCl, TbOCl, and HoOCl show very similar behavior. While $X_{CH4}$ of LaOCl and ErOCl decreases gradually, $S_{CH3Cl}$, $S_{CO}$, and $S_{CH2Cl2}$ are not significantly affected. The largest difference in selectivity of these two catalysts can be observed for LaOCl where $S_{CH3Cl}$ is reduced by 7%. The higher HCl concentration causes CH3Cl to be further chlorinated to CH2Cl2. The additional CH2Cl2 is catalytically destructed, either directly or indirectly via the formation of CHCl3. For GdOCl, TbOCl, and HoOCl, however, larger differences in selectivity are observed, as $S_{CO}$ decreases from 51 to 33% for TbOCl, while $S_{CH4,Cl}$ simultaneously increases from 33 to 52%. GdOCl, TbOCl, and HoOCl are the only catalysts that show an increase in $S_{CH4,Cl}$ with the
increasing HCl concentration. The lower $X_{\text{CH}_4}$ causes less CHCl$_3$ to form (Figure S3A), which is subsequently destructed to CO. The lower activity also affects the degree of methane chlorination and thus lowers the quantity of higher CMs present in the system that can be destructed.33,36

PrOCl and NdOCl fall within the last category having a catalytic activity that is almost completely lost with the increasing HCl concentration. As the activity is correlated to the selectivity observed in the reaction, we observe that $S_{\text{CH}_3\text{Cl}}$ drastically increases. However, $X_{\text{CH}_4}$ (<5%) is too low for commercial use and, therefore, the selectivity observed is irrelevant. The nature of this rapid $X_{\text{CH}_4}$ decrease is not investigated in this study, but it is hypothesized that a completely chlorinated surface inhibits the activation of O$_2$ and/or CH$_4$ by a change in material acidity/basicity. Unlike the other catalyst materials tested in this study, the catalytic performance of EuOCl can be steered by tuning two key parameters, namely, temperature and HCl concentration. The extreme HCl concentrations applied in this study, 10 and 80%, are compared in the temperature range of 350−550 °C. $X_{\text{CH}_4}$ of EuOCl is plotted versus the temperature, as shown in Figure 7A, for the two tested HCl concentrations. Immediately visible is the enhancement of activity from the HCl increase over the entire tested temperature range. Under 10% HCl, the maximum $X_{\text{CH}_4}$ of 38% is reached at 550 °C. The increase in HCl concentration simultaneously lowers the temperature at which the maximum $X_{\text{CH}_4}$ is reached to 505 °C and increases the max $X_{\text{CH}_4}$ to 42%. Furthermore, the observed activity drop is delayed by 20 °C; the nature of this drop will be discussed in Section 3.4. To further demonstrate the remarkable activity increase of
EuOCl upon increasing the HCl concentration, $X_{CH_4}$ is plotted versus the temperature for all catalyst materials at a HCl concentration of 10 and 80%, as shown in Figure S4A,B, respectively. Except for EuOCl, $X_{CH_4}$ of all catalysts was negatively influenced by the increase in HCl concentration over the entire temperature range. This coincides with the results presented in Figure 6, where EuOCl was the only catalyst that showed an increase in $X_{CH_4}$ when increasing the HCl concentration. The maximum $X_{CH_4}$ of all catalysts dropped significantly, for example, from 31 to 19% for TbOCl.

When further comparing the temperature-dependent performance of EuOCl at 10 and 80% HCl concentration, large selectivity differences are observed (Figure 7B,C). $S_{CO}$ is suppressed below 15% at 80% HCl, even at very high conversion levels ($X_{CH_4} \approx 40\%$). To our best knowledge, such a low CO selectivity at high conversion levels is yet unreported and makes the EuOCl material in this study a potential catalyst material for practical applications. The result of the lower CO selectivity is an increase in selectivity toward higher CMs. At 80% HCl concentration and 475 °C, all four CMs are produced. One major drawback from operating the EuOCl system at such high conversion levels is that the selectivity toward CH$_2$Cl thus drastically decreases. The generation of more active sites by fast chlorination due to the excess HCl causes the formed CH$_3$Cl to react further to higher CMs. In that regard, the HCl concentration does not have a significant effect on the CH$_3$Cl selectivity when comparing two different ratios. At 10% conversion, both ratios have $S_{CH_3Cl} = \sim 60\%$ at $X_{CH_4} = 10\%$. CO$_2$ was only detected at high temperatures (>500 °C), and the selectivity was very low (<1.2%).

With such large formations of CH$_2$Cl$_2$ and CHCl$_3$ and noticeable amounts of CCl$_4$ observed at high conversion levels at 80% HCl, thermal chlorination might be a viable route instead of surface-catalyzed reaction. This is supported by the fact that a discrepancy in the product selectivity was observed when comparing 10 and 80% HCl in the feed (Figure 7B,C). A previous work by Pérez-Ramírez and co-workers already investigated the HCl oxidation over EuOCl. Based on these findings, the chemical conversion of methane with Cl$_2$ seems to only have a minor contribution to the total chlorination of methane at the used temperature range in this study. However, the reaction mechanism proposed for LaOCl does not explain how such a high selectivity toward, for example, CHCl$_3$ can be obtained as observed for EuOCl. A previous work by our group already proposed a mechanism where La is shortly reduced by accepting a H from CH$_3$Cl. The proven presence of the redox couple Eu$^{3+}$/Eu$^{4+}$ could participate in the reaction via a similar role, and a mechanism can be proposed for EuOCl where Eu changes the oxidation state during the reaction. Furthermore, the presence of substantial amounts of Eu$^{3+}$ was proven under oxychlorination conditions at $T > 753$ K. To investigate what the contribution of the gas-phase chlorination of methane is to the total catalytic performance of LaOCl and EuOCl, the oxygen conversion ($X_{O_2}$) was determined in a reaction mixture with and without the presence of CH$_4$. The HCl oxidation results are compared to the oxychlorination reaction with the same HCl/O$_2$ feed ratio. For LaOCl (Figure 8A), $X_{O_2}$ was below 5% over the entire tested temperature range. For the oxychlorination reaction over LaOCl, a sharp increase in $X_{O_2}$ is observed from 500 to 550 °C, where $X_{O_2}$ reaches a final value of 35%. As expected from the literature, no Cl$_2$ seems to evolve, and thus, the gas-phase chlorination of methane does not contribute to the overall activity of LaOCl. HCl oxidation over EuOCl was tested at 10 and 80% HCl in the feed (Figure 8B,C respectively), as large differences in activity and selectivity were observed when the HCl concentration was varied. At 10% HCl in the feed, $X_{O_2}$ for the oxychlorination reaction is significantly higher than that for the HCl oxidation over the entire temperature range. However, some consumption of O$_2$ is visible for the HCl oxidation with a maximum $X_{O_2}$ of 13%, thus contributing to the overall performance, although the activity and selectivity are predominantly governed by the surface-catalyzed reaction. The discrepancy between $X_{O_2}$ of the HCl oxidation and MOC reaction is reduced when the HCl concentration is increased to 80%. $X_{O_2}$ of both reactions increased, and the relative difference is decreased. Solely by increasing the HCl concentration, the maximum $X_{O_2}$ is increased from 13 to 55% for the HCl oxidation reaction. The HCl oxidation reaction is accelerated by the large excess of chlorine present on/in the catalyst, and HCl oxidation plays a major role in the overall performance of the catalyst. The large difference in HCl oxidation potency at 10 and 80% HCl also partly explains why the degree of methane chlorination is enhanced when a high HCl concentration is used.

The total product selectivity here is partly governed by the free radical reaction, which offers very limited control over the selectivity. Further research is needed to investigate if the reducibility of Eu$^{3+}$ is enhanced by the excess of HCl. Up till so far, we have demonstrated the excellent performance of EuOCl and compared it to the other catalyst materials reported in this study. However, the reducible CeO$_2$ is arguably the best performing catalyst in MOC with a combined yield of CH$_3$Cl and CH$_2$Cl$_2$ of ~27%. For EuOCl, a remarkable maximum combined yield of 24% is obtained at 485 °C at 80% HCl. We
spectra with 60 min time intervals are given in Figure S6B,D for Figure S6A,C for LaOCl and EuOCl, respectively. Individual Figure 9. The corresponding Raman spectra are 3-D plotted in systems. The results of the sizes), surface area of the active phase,22,47 and/or increasing the rate of both catalysts react differently to a changing HCl concentration in the feed, and hence, detailed characterization studies could provide further insights into the differences between both systems. The results of the operando Raman study are shown in Figure 9. The corresponding Raman spectra are 3-D plotted in Figure S6A,C for LaOCl and EuOCl, respectively. Individual spectra with 60 min time intervals are given in Figure S6B,D for LaOCl and EuOCl materials, respectively. The band attribution is summarized in Table 1.

The spectral data of LaOCl is visualized as a contour plot in Figure 9A. Above the contour plot, the intensity plot of three characteristic vibrations, that is, 217 cm−1 (A1g,B 2g of LaOCl), 341 cm−1 (A1g,B 2g of LaCl3), and 440 cm−1 (Eg of LaOCl), is plotted versus time on stream. From 0–120 min, the catalyst is chlorinated (CH4/HCl/O2/N2/He 0:20:0:1:19 in ml/min) at 450 °C. The fresh LaOCl is rapidly converted into LaCl3 because A1g/B 2g and Eg of LaOCl disappears within several minutes, while 2E2g + A 1g of LaCl3 shows the opposite trend. The intensity of the vibrational modes corresponding to LaOCl do not change significantly after 10 min and disappear in the background. The intensity decrease of the LaOCl vibrational modes and the growth of the LaCl3 vibrational mode at 217 cm−1 occur simultaneously. A rapid increase in peak intensity is observed within the first 10 min after which the Raman vibration intensity growth levels off, as can be seen in the intensity plot. This indicates that LaOCl is almost fully converted into LaCl3 within 15 min of chlorination. From 120–210 min, the catalyst was first heated to 500 °C and a dechlorination step (CH4/HCl/O2/N2/He 2:0:1:1:16) was performed. The dechlorination of the catalyst material was complete after 155 min because A1g/B 2g and Eg of LaOCl reach their final value and 2E2g + A 1g of LaCl3 disappears in the background. No Raman vibration at 408 cm−1, corresponding to La2O3, was observed.41,42 From 210–330 min, a typical oxychlorination reaction mixture (CH4/HCl/O2/N2/He 2:2:1:1:14) was fed into the reactor at 500 °C. No observable spectral changes occur from 210–245 min, which is most probably caused by the phenol catalyst bed height. It is hypothesized that HCl is completely consumed by the top of the
catalyst bed before a steady-state consumption of HCl is reached and HCl travels further through the catalyst bed. Here, a more gradual transition between LaOCl to LaCl3 is observed, starting after 270 min. As already expected from the chlorination and dechlorination steps, the rate of chlorination exceeds the rate of dechlorination. After 330 min, vibrational modes corresponding to LaOCl and LaCl3 are both visible, indicating that the catalyst material is in between a LaOCl–LaCl3 state. However, at the end of the experiment, the intensity of the LaOCl bands almost disappeared in the background (Figure S6B). At 330 min, the catalyst is composed of almost pure LaCl3 and it is expected that the remaining LaOCl would be converted to LaCl3 over prolonged reaction times. Thus, even at low HCl concentrations (10%), the chlorination rate of the catalyst material exceeds the dechlorination rate.

The same chlorination–dechlorination–oxychlorination experiment was performed for the EuOCl material. The spectral data of EuOCl are visualized as a contour plot in Figure 9B. Above the contour plot, the intensity of three vibrations at 228 cm$^{-1}$ (2E$_{2g}$ + A$_g$ of EuCl3), 357 cm$^{-1}$ (A$_{1g}$, B$_{2g}$ of EuOCl), and 489 cm$^{-1}$ (E$_g$ of EuOCl) is plotted versus the time on stream. In the Raman spectrum of EuOCl, two bands at 282 cm$^{-1}$ ($\lambda = 540$ nm) and 423 cm$^{-1}$ ($\lambda = 544$ nm) cannot be ascribed to Raman vibrations. These peaks most likely correspond to the $^3\text{D}_1 \rightarrow ^1\text{F}_{0\,\frac{1}{2}}$ ($\lambda = 525$–$584$ nm) emission lines of Eu$^{3+}$.$^{50,51}$ From 0–120 min, a gradual decrease of all Raman vibration intensities is observed and it appears that the final state is only reached after 50 min of reaction. Considering that LaOCl was fully chlorinated to LaCl3 within 15 min, it can be stated that EuOCl is less susceptible to chlorinate into LnCl3 than LaOCl. The typical vibration of EuCl3 at 228 cm$^{-1}$ also decreases in intensity because it overlaps with the more intense 282 cm$^{-1}$ emission line, which decreases over time. The observed intensity of the EuCl3 vibration at the tested temperature is very weak (Figure S6D), probably due to the weakening of the Eu–Cl bond and the loss of coordination number near $T_{\text{melts}}$. Not only is the Raman signal lost upon chlorination, but the photoluminescence signal of EuCl3 is also quenched upon heating. In Figure S7A,B, a temperature ramp on EuOCl/EuCl3 was performed. A gradual change from the EuCl3 spectrum to the EuOCl spectrum is observed, heating from 20 to 350 °C. No difference can be observed between the reference EuOCl and the EuOCl/EuCl3 spectrum (Figure S7C), even though the composition of the heated sample did not change during the temperature ramp (Figure S7D). The loss of the signal, both in the Raman and photoluminescence spectra, indicates the chlorination of EuOCl to EuCl3. Hence, the photoluminescence intensity is directly correlated to the degree of catalyst chlorination. From 120–210 min, the intensity of all Raman bands is restored during the dechlorination. Again, the Raman signal of the $2\text{E}_{2g}$ + A$_g$ vibration of EuCl3 at 235 cm$^{-1}$ increases due to the rise of the relatively broad 282 cm$^{-1}$ emission line. No formation of Eu$_2$O$_3$ was observed, as its distinct vibration at 345 cm$^{-1}$ was not detected.$^{52,53}$ From 210–330 min, the Raman spectra did not change during the oxychlorination step. A small variation in peak intensity was observed in the beginning of the experiment, but from the intensity plot, it is apparent that no major changes occurred. Hence, little bulk chlorination takes place. The high rate of methane chlorination, and thus surface dechlorination, results in that EuOCl does not bulk chlorinate. Evident from the reaction mechanism (Figure 5) is that the surface chlorination must occur for the reaction to take place. In combination with the fact that the activity is increased with the increasing HCl concentration, we can conclude that the surface chlorination is rate-limiting and not the activation of O$_2$ or CH$_4$. An increase in the HCl concentration is therefore beneficial for the catalytic activity of EuOCl because surface chlorination occurs more readily.

### 3.4. Operando Photoluminescence Spectroscopy

Both activity profiles of EuOCl shown in Figure 7A show a similar behavior, as both profiles show a drop in the activity after which the activity is restored at higher temperatures. At 10% HCl, the onset of the drop occurs at ~475 °C and the minimum is reached at ~500 °C. At 80% HCl, the onset of the drop is delayed from 480 to 500 °C and a maximum $X_{\text{CH}_4}$ of 42% is reached. At 550 °C, EuOCl reaches the same $X_{\text{CH}_4}$ of ~38% for both conditions. As this drop is reproducible with different newly synthesized EuOCl catalysts and for the same EuOCl catalyst when the same experiment is repeated, we investigated the role of the degree of catalyst chlorination on the drop in activity. Temperature ramp experiments from 450 to 520 °C were performed with the same catalyst, but the pretreatment step was varied. Furthermore, photoluminescence spectra of EuOCl were collected with the operando Raman probe. The collected spectra were normalized to the highest signal of the series and integrated over the entire spectral range. The relative spectral area is used as a measure for the degree of chlorination, as the chlorination of EuOCl to EuCl3 quenches the signal, as described in Section 3.3. The $X_{\text{CH}_4}$ and relative spectral area are plotted versus the temperature. In Figure 10A, standard oxychlorination at 450 °C was applied as a pretreatment step (CH$_4$/HCl/O$_2$/N$_2$/He 2:2:1:1:14). $X_{\text{CH}_4}$ increases linearly with...
the increasing temperature, while the opposite trend is observed for the relative spectral area. No spectral changes occurred during the temperature ramp, and only the intensity of the signal decreased with the increasing temperature. The gradual decrease in the relative area is expected, as the overall photoluminescence intensity is negatively correlated with the temperature. Subsequently, the catalyst was cooled to 450 °C and chlorinated for 2 h prior to the temperature ramp (CH4/HCl/O2/N2/He 0:4:0:1:15), as shown in Figure 10B. Now, the drop in activity is observed, starting at 500 °C, which coincides with the temperature of the drop observed in Figure 7A for EuOCl tested at 80% HCl. The sharp decrease in activity and the exponential growth of the relative spectral area occur simultaneously, indicating that bulk EuCl3 is rapidly converted to EuOCl, as mostly the state of the catalyst bulk is probed with photoluminescence spectroscopy. Both XCH4 and the relative spectral area stabilize at 515 °C, indicating that the catalyst reaches a steady state. The reaction temperature plays a crucial role in the degree of catalyst chlorination. In a scenario where excess HCl is present in the feed, bulk chlorination occurs at lower temperatures. Once the temperature is increased to >480 °C, bulk chlorination becomes unfavorable, and the bulk chlorine migrates to the surface, temporarily increasing the degree of surface chlorination. Hence, an increase in the activity is observed, as chlorine is forced out of the catalyst. Once the free chlorine in the catalyst depletes, activity and selectivity are restored to the same levels as observed when no drop in activity was observed. The pretreatment step as shown in Figure 10A,B additionally reveals that the presence of methane also plays a vital role in the degree of catalyst chlorination. Figure 8B shows the HCl oxidation rate at 450 °C and 10% HCl is low, and dechlorination of the catalyst via HCl oxidation is thus a slow process. Furthermore, the HCl oxidation rate is limited by the HCl concentration in the feed, as the rate could be significantly enhanced when excess HCl was fed (Figure 8C). In Figure 10, we showcase that with and without the presence of methane in the feed, the catalyst is either in a dechlorinated or in a chlorinated state, respectively. We can therefore conclude that the state of the catalyst is determined by both the reaction temperature and the HCl/CH4 ratio in the feed.

3.5. Stability of EuOCl. Finally, EuOCl was tested for its stability under oxychlorination conditions at 450 °C. Over a period of 48 h, the catalyst was exposed to increasing HCl concentrations with constant CH4 and O2 concentration and total flow. The XCH4 product yields and reaction selectivity are plotted in Figure 11A. At the start, a drop in XCH4 and yields of CH3Cl and CO are visible. This effect is most probably caused by the decrease in the surface area of the catalyst because no prechlorination step was performed.22 After 2 h of reaction, the CH3Cl yield stabilizes, while the CO yield gradually decreases. This is also visible from the selectivity plot shown in Figure 11A where SCO decreases from 44 to 37%, while SCH3Cl increases with the same percentage and SCH2Cl remains the same. Subsequently, the HCl concentration was increased to 20% without increasing the total flow. An immediate jump in CH3Cl (+2.2%), CH2Cl2 (+0.6%), and CO (+0.8%) yield occurs due to the increased chlorination rate of the catalyst surface. However, now, the CH3Cl yield drops over time (−0.8%), while the CO yield remains constant.

Figure 11. (A) XCH4, and SCH3Cl, SCH2Cl2, SCHCl3, SCCl4, SCO, and SCO2 plotted vs time on stream and (B) operando Raman spectra plotted vs time on stream between 38 and 42 h. The vertical lines in (B) are plotted individually in (C) to show the loss of Raman peak intensity of the vibrations corresponding to EuOCl.
Again, a jump in yield is observed when increasing the HCl concentration to 40% for CH₃Cl (+2%), CH₂Cl₂ (+1.1%), and CO (+1%). The selectivity of all the products remains fairly constant over the duration of 10 h. The yields of the reaction products decrease slightly. Up to this point, the catalyst material behaves in the same fashion. However, when the HCl concentration is further increased from 40 to 60%, a different catalytic behavior is observed.

Right from the moment that the HCl concentration was further increased, the CO yield drops gradually (−1.1%), while the CM yields do not show any downward trend. S₃CO is reduced from 26 to 20%, a relative decrease of 23%. Under these conditions, we observe a low CHCl₃ yield of 0.4%, which correlates to a S₂CHCl from 2.4%. Near the end, the production of CH₂Cl increases slightly after which it starts to drop when the HCl concentration is further increased to 80%.

Just before the feed ratio is adjusted to 80% HCl, we observe a change of the catalytic property, as analyzed with operando Raman spectroscopy. The operando Raman spectra in the spectral range of 180−500 cm⁻¹ are plotted versus the time on stream in Figure 11B. Furthermore, some individual operando Raman spectra are plotted of moments before and after changing the feed ratio to 80% HCl in Figure 11C. After 38 h time on stream, the Raman spectra start to change and the overall intensity decreases, which are indicative of the transition from EuOCl to EuCl₃.

The full chlorination of the catalyst material has severe effects on the catalytic behavior. While the selectivity of the reaction does not seem to be affected by the changing catalyst properties, the catalyst deactivates. The decreasing CO yield trend is continued, but the CH₃Cl yield is negatively affected over time. From previous experiments, we proved that EuOCl was difficult to chlorinate, especially under oxychlorination conditions. We now show that bulk transformation of EuOCl to EuCl₃ occurs under very high HCl concentrations (≥60%) over prolonged reaction times. Moreover,bulk chlorination is unwanted because a decrease in the product yield was observed. A balanced HCl concentration in the feed mixture is therefore crucial to enhance the surface chlorination rate but also to prevent bulk chlorination. An HCl concentration between 40 and 60% appears to be optimal, in terms of catalyst stability and catalytic performance.

4. CONCLUSIONS

We have investigated a series of lanthanide oxide chlorides (i.e., LnOCl with Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, or Ho) and Er- and Yb-based catalyst materials, which turned to be all active in the catalytic oxychlorination of CH₄. Based on their catalytic activity, the following ranking can be made as follows: Eu > Tb > Gd > Ho ∼ Er ∼ Dy > Sm > Pr ≈ Nd ≈ La ≈ Yb. Furthermore, from all the catalyst materials under investigation, EuOCl exhibited the highest activity and the best selectivity toward CH₃Cl. The catalytic performance of EuOCl could be further increased by altering the HCl concentration, as an excess of HCl doubled the activity and lowered the CO selectivity. Exceptionally high conversion levels (∼40%) could be reached, while maintaining a low CO₂ selectivity (<1%). Operando Raman spectroscopy revealed that the surface chlorination of the catalyst surface is rate-limiting, and hence, the activity of both the MOC and the HCl oxidation is boosted when an excess HCl is present. Operando photoluminescence spectroscopy of Eu³⁺ revealed that the bulk of EuOCl was subjected to major changes, and the state of the catalyst is determined by the CH₄/HCl ratio. However, if high HCl concentrations are applied at low X₄H, over prolonged reaction times, EuOCl does chlorinate fully and the catalyst activity is lowered. The tunable activity and selectivity by altering the HCl concentration in the feed and the reaction make EuOCl a very interesting candidate as a catalytic material for a viable CH₄ oxychlorination process.
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