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Lanthanide compounds as catalysts for the one-step synthesis of vinyl chloride from ethylene

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1 Abstract

2 The industrial manufacture of vinyl chloride relies on a two-step process involving CuCl₂-catalyzed ethylene oxychlorination to ethylene dichloride followed by thermal cracking of the latter to vinyl 3 chloride. This work evaluates a wide range of commercial and self-prepared lanthanide (La, Ce, Pr, 4 Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er) compounds for the one-step production of vinyl chloride from 5 ethylene in a fixed-bed reactor at 623-773 K and 1 bar using feed ratios of C₂H₄:HCI:O₂:Ar:He = 3-6 6:1-9.6:1-7:3:80-92 and space times of 6-252 g h mol⁻¹ (based on ethylene). Ex situ 7 characterization by X-ray diffraction, electron microscopy, and X-ray photoelectron spectroscopy 8 reveal that the oxide forms of all compounds, except CeO₂, transform into their respective 9 (oxy)chloride. Among all studied systems, CeO₂ shows the highest activity but suffers from 10 combustion forming COx, while europium oxychloride (EuOCI) leads to the best vinyl chloride 11 selectivity of 96% at 20% C₂H₄ conversion for over 100 h on stream. Temperature-programmed 12 reduction with H₂, temperature-programmed desorption of NH₃, and oxidation tests (C₂H₄, CO, and 13 14 HCl oxidation) unravel the unique balance of mild redox and enhanced acid properties of EuOCl compared to CeO₂, which suppress over-oxidation and boost ethylene 15 dichloride dehydrochlorination. Strategies to couple the excellent selectivity of EuOCI with the high activity of 16 CeO_2 are demonstrated through the synthesis of homogeneous europium-cerium mixed oxides, 17 18 combining two functions on a single surface. In addition, the engineering of a dual-bed reactor, integrating a CeO₂ bed first to produce ethylene dichloride in high yield which is subsequently 19 transformed to vinyl chloride over EuOCI leads to vinyl chloride yields of up to 30% per pass. 20 These very promising findings constitute a crucial step for process intensification of polyvinyl 21 chloride production and exploring the potential of rare-earth compounds in industrially-relevant 22 23 reactions.

24

Keywords: ethylene oxychlorination, lanthanides, europium oxychloride, vinyl chloride monomer,
 bifunctional catalyst, process intensification

1 **1. Introduction**

2 Polyvinyl chloride (PVC, 44 Mton, annual global growth rate of 3.2%) is an integral part of modern society owing to its widespread applications that improve our everyday life [1,2]. Its 3 4 monomer, chloroethene (commonly known as vinyl chloride and hereafter denoted as VCM), 5 was first produced on a commercial scale in the 1920s through acetylene hydrochlorination 6 over mercuric chloride catalysts, which still is the main production method in countries such 7 as China, due to cheap availability of coal from which acetylene is produced [3,4]. However, the increasing demand for PVC and rising price of acetylene in the late 1950s prompted a 8 shift in the feedstock to the more economical ethylene in the United States and Europe [3]. 9 10 Since then, VCM is predominantly produced via a two-step process involving the selective oxychlorination of ethene (commonly known as ethylene) to 1,2-dichloroethane (commonly 11 known as ethylene dichloride and hereafter denoted as EDC) over promoted CuCl₂/γ-Al₂O₃ 12 catalysts in fluidized-bed reactors (T = 473-573 K, P = 1-10 bar) and the subsequent thermal 13 cracking of EDC to VCM (T = 773-873 K, P = 25-35 bar) [3,4,5]. The greatest limitations of 14 the current process are the stability issues faced by the copper catalyst, and the limited per 15 16 pass conversion (50-60% with VCM selectivity > 98%) and high energy demand of the thermal cracking [3]. Despite continued efforts to optimize the robustness of the catalyst by 17 doping with additives such as alkali (Li, Na, K), alkaline earth (Mg, Ca), and rare earth 18 metals (La, Ce), the copper chloride phase is still prone to volatilization and particle 19 20 agglomeration [6-10]. Besides, the possible intensification of VCM production by integration of the oxychlorination and dehydrochlorination reactions as a one-step process requires a 21 novel catalyst which can combine two functions. 22

In order to achieve this goal, new materials such as non-halide copper containing catalysts [11] and lanthanide (oxy)chlorides [12], particularly lanthanum oxychlorides, have been reported in the patent literature. However, none of these systems is realized on an industrial scale, most likely due to the low per pass VCM yields and/or stability hurdles faced by these catalysts. Recently, we have uncovered the high stability and remarkable yield of

chlorinated compounds (25% VCM, 25% EDC) over CeO₂. This outstanding performance
was attributed to the integration of both redox sites, which catalyze the ethylene
oxychlorination to EDC, and acid sites, responsible for the dehydrochlorination of EDC to
VCM, on the same catalyst surface.

5 In spite of these encouraging results, CeO₂ offers significant margins for improvement. In particular, a considerable amount of over-chlorinated compounds (1,2-dichloroethene, 6 7 commonly known as 1,2-dichloroethylene and hereafter denoted as 1,2-DCE) and 8 combustion products (CO_x) were also formed, decreasing the overall selectivity of EDC and 9 VCM. Moreover, only moderate dehydrochlorination activity was observed. Thus, it can be 10 anticipated that materials exhibiting milder oxidative properties and higher density of strong 11 cites than ceria could lead to enhanced performance. Surprisingly, despite their extensive use as dopants of the CuCl₂/₂-Al₂O₃ catalysts, lanthanide compounds were never 12 systematically investigated as the main active phase for the conversion of ethylene to VCM. 13 14 Besides, they were investigated in several other catalyst formulations mainly as dopants and 15 supports [14-18], with the exception of cerium oxide and lanthanum oxide (or (oxy)chloride) which are also studied as the primary catalytic phase in oxidative processes, including CO 16 17 oxidation [19,20], isobutane oxidation [21], HCl oxidation [22,23], methane oxidative coupling [24], selective reduction of nitrogen oxides [19,25], and methane oxychlorination [26,27]. 18

19 Herein, the comparison of the performance of a broad set of the most abundant rareearth compounds leads to the discovery of the exceptional performance of europium 20 oxychloride, exhibiting 96% VCM selectivity at 20% conversion for over 100 h on stream. 21 22 Structural, redox, and acidic properties are investigated to rationalize the superior 23 performance of europium oxychloride with respect to other lanthanides and parametric studies give insight to the distribution of products. In order to attain superior VCM yields, this 24 novel active phase is combined with the high activity of CeO₂ by synthesis of mixed oxides 25 and through dual-bed reactor concepts. This study comprises the first practically-relevant 26 application of europium in heterogeneous catalysis and the materials presented here have 27

great potential to be explored in challenging catalyzed reactions, particularly towards the
 functionalization of hydrocarbons.

3

4 **2. Experimental methods**

5 2.1. Catalyst preparation

6 Commercial La₂O₃ (Alfa Aesar, 99.99%), Pr₂O₃ (Alfa Aesar, 99.9%), Nd₂O₃ (Sigma-7 Aldrich, 99.9%), Sm₂O₃ (Sigma-Aldrich, 99.9%), Eu₂O₃ (Sigma-Aldrich, 99.5%), Gd₂O₃ (Alfa Aesar, 99.99%), Tb₂O₃ (Strem Chemicals, 99.9%), Dy₂O₃ (ABCR, 99.99%), Ho₂O₃ (Fluka 8 Chemie, 99.9%), and Er₂O₃ (Fluka Chemie, 99.9%) were calcined at 773 K, and CeO₂ 9 10 (Sigma-Aldrich, 99.9%) at 773 K and 1173 K in static air using a heating rate of 5 K min⁻¹ and an isothermal step of 5 h prior to their use in catalytic studies. Analysis by X-ray 11 diffraction revealed that the commercial praseodymium oxide actually consisted of Pr₄O₇ and 12 thus it is denoted as such herein. Europium oxide (Eu₂O₃-p- T_{cal} , where T_{cal} denotes the 13 14 calcination temperature in K), cerium oxide (CeO₂-p- T_{cal}), and mixed europium-cerium oxides (Eu_xCe_{1-x}O_{2-0.5x}-cp- T_{cal} , where x represents the molar fraction of Eu in the range of 15 0.3-0.9) were synthesized by precipitation (p, single oxides) and coprecipitation (cp, mixed 16 oxides) following a protocol reported elsewhere [13]. Briefly, the metal nitrates 17 (Eu₂(NO₃)₃·6H₂O (ABCR, 99.9%) for Eu₂O₃-p, Ce(NO₃)₃·6H₂O (ABCR, 99.9%) for CeO₂-p, or 18 mixtures for $Eu_xCe_{1-x}O_{2-0.5x}$ -cp) were dissolved in deionized water under stirring and H_2O_2 19 (Acros Organics, 35%) was added to the solution to obtain a molar H_2O_2 : M ratio of 3 20 (M = Eu, Ce, or Eu+Ce). The coprecipitation was achieved by the dropwise addition of 21 22 aqueous NH₄OH (Sigma-Aldrich, 30%) until a pH of 10.5 was reached. The slurry was stirred for 4 h and washed with deionized water. Upon filtration, the precipitate was dried at 23 393 K for 12 h and calcined at 773 K for CeO₂-p, 773-1173 K for Eu₂O₃-p, and 773 K for 24 Eu_xCe_{1-x}O_{2-0.5x}-cp in flowing air using a heating rate of 5 K min⁻¹ and an isothermal step of 25 5 h. 26

27

2.2. Characterization

The metal content was determined by X-ray fluorescence (XRF) spectroscopy using an 2 Orbis PC Micro-EDXRF analyzer with a Rh source (15 kV, 500 µA) and a silicon drift 3 detector. Powder X-ray diffraction (XRD) was measured using a PANalytical X'Pert PRO-4 MPD diffractometer and Cu-K α radiation ($\lambda = 0.15418$ nm). The data was recorded in the 5 10-70° 2θ range with an angular step size of 0.017° and a continuing time of 0.26 s per step. 6 N₂ sorption at 77 K was measured in a Quantachrome Quadrasorb-SI analyzer. Prior to the 7 measurements, the samples were outgassed to 50 mbar at 573 K for 3 h. The Brunauer-8 9 Emmett-Teller (BET) method [28] was applied to calculate the total surface area, S_{BET} , in 10 m² g⁻¹. High-resolution transmission electron microscopy (HRTEM) and elemental mapping using energy-dispersive X-ray spectroscopy (EDX) were conducted on a FEI Talos 11 microscope operated at 200 kV. All samples were dispersed as dry powders onto lacey 12 13 carbon coated nickel or molybdenum grids. X-ray photoelectron spectroscopy (XPS) 14 measurements were performed on a Physical Electronics Quantum 2000 X-ray 15 photoelectron spectrometer using monochromatic Al-K α radiation generated from an electron beam operated at 15 kV, and equipped with a hemispherical capacitor electron-16 energy analyzer. The powdered sample was firmly pressed onto the foil. The area analyzed 17 was 150 µm in diameter and the electron take-off angle was 45°. The pass energy used for 18 the detailed spectra of the C1s, O1s, Cl2p, Eu3d, Eu4d, and Ce3d core levels was 19 46.95 eV to yield a total analyzer energy resolution of 0.95 eV. The spectrometer energy 20 scale was calibrated for the Au 4f electrons to be at 84.0±0.1 eV. Partial compensation of 21 22 surface charging during spectra acquisition was obtained by the simultaneous operation of electron and argon ion neutralizers. Elemental concentrations are given in atomic percent 23 24 using the measured photoelectron peak areas after Shirley background subtraction and the built-in sensitivity factors for calculation. Temperature-programmed desorption of ammonia 25 (NH₃-TPD) and temperature-programmed reduction with hydrogen (H₂-TPR) were performed 26 27 using a Micromeritics Autochem II 2920 unit equipped with a thermal conductivity detector

1 coupled to a MKS Cirrus 2 mass spectrometer. The powder sample (0.1 g) was loaded into a U-shaped quartz micro-reactor, pretreated in He (20 cm³ STP min⁻¹) at 573 K for 3 h, and 2 cooled to 373 K in He. For NH₃-TPD experiments, ammonia was chemisorbed at 473 K in 3 three consecutive cycles of saturation with 5 vol.% NH₃/He (20 cm³ STP min⁻¹) for 30 min 4 5 followed by purging with He (20 cm³ STP min⁻¹) at the same temperature for 30 min. Desorption of NH₃ was monitored in the range of 473-1273 K using a heating rate of 6 20 K min⁻¹ and a He flow of 20 cm³ STP min⁻¹. For H₂-TPR experiments, the sample was 7 pretreated in He (20 cm³ STP min⁻¹) at 423 K for 1 h, and cooled to room temperature 8 followed by ramping the temperature at 10 K min⁻¹ up to 1273 K in 5 vol.% H₂ 9 $(20 \text{ cm}^3 \text{ STP min}^{-1}).$ 10

11

12 2.3. Catalytic tests

13 The gas-phase oxychlorination of ethylene was investigated at ambient pressure in a continuous-flow fixed-bed reactor (Scheme 1). The set-up consists of (i) mass flow 14 controllers to feed C₂H₄ (PanGas, 20.15% in He), HCl (Air Liquide, purity 2.8, anhydrous), O₂ 15 (Messer, 10.06% in He), He (PanGas, purity 5.0) as a carrier gas, and Ar (PanGas, purity 16 17 5.0) as an internal standard, (ii) a syringe pump (Nexus 6000, Chemyx) to feed EDC (Fluka, 99.5%), (iii) a vaporizer operated at 403 K accommodating a quartz T-connector filled with 18 glass beads to vaporize EDC, (iv) an electrically heated oven hosting a quartz micro-reactor 19 equipped with a K-type thermocouple whose tip reaches the center of the catalyst bed, (v)20 downstream heat tracing to avoid any condensation of the reactants and products, and (vi) a 21 gas chromatograph coupled to a mass spectrometer (GC-MS) for on-line analysis. The 22 effluent stream was neutralized by passing it through an impinging bottle containing an 23 aqueous NaOH solution (1 M). The catalyst ($W_{cat} = 0.25-2$ g, particle size, $d_p = 0.4-0.6$ mm) 24 was loaded in the micro-reactor (10 mm inner diameter) and pretreated in He at 473 K for 25 30 min. Thereafter, a total flow (F_T) of 100 cm³ STP min⁻¹ containing 3-6 vol.% C₂H₄, 1-26 9.6 vol.% HCl, 1-7 vol.% O₂, and 3 vol.% Ar as internal standard, balanced in He was fed to 27

the reactor at a bed temperature (T) of 623-773 K and pressure (P) of 1 bar. Note that 1 relatively low feed concentrations were selected to prevent corrosion, enable safe handling, 2 3 and minimize the formation of hot spots in the catalyst bed due to the high reaction 4 exothermicity. Temperature measurements in a reference experiment on CeO₂-1173 (at 31% C₂H₄ conversion), evidenced a temperature gradient of 0.9 K across the bed when the 5 temperature in the center of the catalyst bed was set to 673 K (Scheme 1). The standard 6 conditions of 3 vol.% C₂H₄, 4.8 vol.% HCl, and 3 vol.% O₂ were chosen based on the 7 8 literature [8,13]. The space time, defined as the ratio of the catalyst mass and the inlet molar flow of ethylene as the limiting reactant, $W_{cat}/\dot{n}^0(C_2H_4)$ was varied in the range of 6-9 252 g h mol⁻¹. In the dehydrochlorination tests, 1.5 vol.% EDC was fed to the catalyst 10 $(W_{\text{cat}} = 0.5 \text{ g}, d_p = 0.4-0.6 \text{ mm})$ using He as carrier gas $(F_T = 100 \text{ cm}^3 \text{ STP min}^{-1})$ with or 11 without addition of HCl (4.8 vol.%) and O₂ (3 vol.%) at T = 523-773 K and 12 13 $W_{\rm cat}/\dot{n}^0$ (EDC) = 126 g h mol⁻¹. Prior to the analysis of the reaction mixtures, the catalysts were equilibrated for at least 1 h under each condition. The gas composition at the reactor 14 outlet containing reactants (C₂H₄, O₂, HCl) and products (EDC, VCM, 1,2-DCE, CO, CO₂) 15 was analyzed online using a gas chromatograph equipped with a GS-CarbonPLOT column 16 17 coupled to a mass spectrometer (Agilent GC 7890B, Agilent MSD 5977A) with a triple-axis detector and an electron multiplier. A representative chromatogram is depicted as an inset in 18 **Scheme 1**. In the oxidation tests, C_2H_4 (3 vol.%), CO (2.5 vol.%), or HCI (3 vol.%) and O_2 19 were fed in a 1:1 volumetric ratio. In the HCl oxidation tests, the Cl₂ production was 20 quantified by offline iodometric titration (using a Mettler Toledo G20 Compact Titrator) of 21 triiodide, formed by purging the Cl₂ containing reactor outlet through an aqueous KI (Sigma-22 Aldrich, 99.5%) solution (0.1 M), with 0.01 M sodium thiosulfate solution (Sigma-Aldrich, 23 99.99%). The conversion of HCI, X(HCI), was calculated using Eq. 1, 24

$$X(\text{HCI}) = \frac{2x_{\text{Cl}_2,\text{outlet}}}{x_{\text{HCI,inlet}}} \cdot 100,\%$$
(Eq. 1)

where $x_{\text{HCl,inlet}}$ and $x_{\text{Cl}_2,\text{outlet}}$ denote the volumetric concentration of HCl and Cl₂ at the reactor inlet and outlet, respectively. The conversion of carbon containing reactant, *X*(*i*), where *i* denotes C₂H₄ or CO, was calculated according to **Eq. 2**,

4

$$X(i) = \frac{x_{i,\text{inlet}} - x_{i,\text{outlet}}}{x_{i,\text{inlet}}} \cdot 100,\%$$
(Eq. 2)

where $x_{i,inlet}$ and $x_{i,outlet}$ denote the volumetric concentration of *i* at the reactor inlet and outlet, respectively. The selectivity and yield of a reaction product *j*, *S*(*j*) and *Y*(*j*), were calculated according to **Eqs. 3 and 4**,

8

$$S(j) = \frac{x_j / v_j}{\sum x_j / v_j} \cdot 100, \%$$
 (Eq. 3)

9

10

 $Y(j) = \frac{X(i) \cdot S(j)}{100}, \%$ (Eq. 4)

where x_j and v_j denote the volumetric concentrations of product *j* at the reactor outlet and the corresponding stoichiometric factor with respect to the number of carbon atoms, respectively (*e.g.*, $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$, $v_{CO} = 2$). The rate of VCM production, *r*(VCM), and the rate of ethylene consumption, *r*(C_2H_4) were calculated using **Eq. 5 and 6**,

15
$$r(VCM) = \frac{x_{C_2H_4,\text{inlet}} \cdot F_T \cdot X(C_2H_4)/100 \cdot P \cdot S(VCM)/100}{R \cdot T_{STP} \cdot W_{cat} \cdot S_{BET}}, \text{ mol } h^{-1} \text{ m}^{-2}$$
(Eq. 5)

16

17
$$r(C_{2}H_{4}) = \frac{x_{C_{2}H_{4},\text{inlet}} \cdot F_{T} \cdot X(C_{2}H_{4})/100 \cdot P}{R \cdot T_{\text{STP}} \cdot W_{\text{cat}} \cdot S_{\text{BET}}}, \text{ mol } h^{-1} \text{ m}^{-2}$$
(Eq. 6)

18 where $x_{C_2H_4,inlet}$, R, and T_{STP} , denote volumetric reactor inlet C_2H_4 concentration, gas 19 constant, and temperature at standard conditions, catalyst mass, and specific surface area, 20 respectively. The carbon mass balance error ε_c was determined using **Eq. 7**,

21
$$\varepsilon_{\rm C} = \left| \frac{\sum x_{i,j,\text{inlet}} / v_{i,j,\text{inlet}} - \sum x_{i,j,\text{outlet}} / v_{i,j,\text{outlet}}}{\sum x_{i,j,\text{inlet}} / v_{i,j,\text{inlet}}} \right| \cdot 100, \%$$
(Eq. 7)

where $x_{i,j}$ and $v_{i,j}$ denote the concentration of reactant *i* or product *j* at the reactor inlet or outlet and the corresponding stoichiometric factor with respect to the number of carbon atoms, respectively. Each catalytic data point reported is an average of at least three measurements. The carbon mass balance in all catalytic tests closed at 96% or higher. After the tests, the catalyst bed was quenched to room temperature in He flow.

1 **3. Results and discussion**

2 **3.1.** Performance of lanthanide compounds in ethylene oxychlorination

3 The lanthanide oxides evaluated in this study were characterized by XRF (Fig. S1) and XRD (Fig. S2) to confirm their compositional and phase purity. All results coincided with the 4 manufacturers specifications except in the case of praseodymium, which was found to be 5 6 present mainly in the form of Pr₄O₇ rather than Pr₂O₃. Besides, the post-reaction structural 7 analysis revealed that all samples except CeO₂ undergo phase transitions to their respective (oxy)chloride phase (vide infra; e.g. Eu₂O₃ transforms to EuOCI). For this reason, the 8 catalysts are denoted according to the crystalline phase evidenced by XRD in the 9 10 equilibrated materials (after treatment for at least 1 h under reaction conditions).

11 Comparative assessment in ethylene oxychlorination (Fig. 1), revealed that the rare earth materials can be classified into three groups according to their performance. The first 12 (SmOCI, ErCl₃, TbOCI, and HoOCI) and second (PrOCI, DyOCI, GdOCI, NdCl₃, LaCl₃) both 13 14 display only minor activity, and are differentiated by the observation of chlorinated products (EDC or VCM) which are only formed over the latter group. In contrast, the third group, 15 comprising CeO₂ and EuOCI, stands out, exhibiting notably higher C₂H₄ conversion and 16 selectivity to chlorinated products than either of the other groups. CeO₂, which was 17 18 previously studied in this reaction, demonstrated the highest yield of chlorinated compounds. On the other hand, EuOCI interestingly showed the highest selectivity to VCM (51% versus 19 30% over CeO₂ at 12 and 26% C₂H₄ conversion, respectively) and no formation of CO₂. Two 20 advantageous features of EuOCI can be highlighted: the suppressed CO_2 formation 21 22 indicates an inherently lower reducibility of EuOCI with respect to CeO₂ while still maintaining the ability to form EDC and the low EDC selectivity over EuOCI evidences that 23 more than 90% of the EDC formed is directly transformed to VCM. In addition, EuOCI shows 24 a 1.5 fold higher relative ethylene conversion per unit surface area of the equilibrated sample 25 as determined by N_2 sorption (Table 1) than CeO₂. In fact, comparison of the surface 26

normalized rate of VCM production as a function of the inverse of temperature (Fig. 1, inset)
 reveals that EuOCI outperforms CeO₂ in the whole temperature range.

Previously [13], we showed that the ethylene oxychlorination performance of CeO_2 could 3 4 be enhanced through the preparation of materials with higher surface areas by precipitation. 5 Following this strategy, a series of europium-based catalysts (EuOCI-p- T_{cal} , where T_{cal} 6 denotes the calcination temperature) were prepared with surface areas comparable to that of 7 CeO₂. Surprisingly, however, these samples did not lead to the expected increase in 8 conversion, but completely suppressed the oxidation reaction to CO and largely increased 9 the yields of EDC and VCM (Fig. 1), which were highest over EuOCI-p-973. In this case, 10 EuOCI-p-973 was found to be one order of magnitude more reactive than CeO₂ and 11 comparable to EuOCI in terms of surface normalized rate (Fig. 1, inset).

12

13 **3.2. Catalyst evolution in ethylene oxychlorination**

Analysis of the structure, composition, porosity, and surface properties of the equilibrated 14 catalysts provides insight into the trends observed during the comparative evaluation in 15 ethylene oxychlorination. As mentioned (vide supra), phase transformations were observed 16 17 in all of the catalysts after evaluation in the ethylene oxychlorination reaction, except CeO₂. Nonetheless, this phase evolution should be regarded as an equilibration step leading to the 18 successful formation of the active (oxy)chloride phase rather than proof of instability. In fact, 19 no catalyst volatilization was evidenced. Comparison by XRD (Figs. 2, S2) identifies three 20 different degrees of transformation, encompassing the preservation of the bulk oxide (CeO₂) 21 [13,22], the formation of an oxychloride (SmOCI, TbOCI, HoOCI, PrOCI, EuOCI), and the 22 complete transformation to the chloride phase (ErCl₃, NdCl₃, LaCl₃). Despite exhibiting 23 distinct performance, only a single europium oxychloride phase is observed in EuOCI-p-973 24 and EuOCI. Slightly sharper reflections in the latter reflect increased average particle size, 25 which is in line with lower surface area. A Scherrer-based analysis confirms an average 26 crystal size of 31 nm for EuOCI in comparison with 13 nm for the EuOCI-p-973 sample. 27

1 Examination of LaCl₃, EuOCl, and CeO₂ by TEM and elemental mapping clearly revealed the different extent of chlorination in these samples. LaCl₃ (Fig. 3a), which fully chlorinates 2 3 upon equilibration under ethylene oxychlorination conditions, comprises large agglomerates 4 of between 100-200 nm diameter. The relative intensity of the CI and La lines in the EDX 5 spectrum of *ca.* 3 agrees well with the stoichiometry of the metal chloride. Comparatively, 6 EuOCI as well as EuOCI-p-973 (Fig. 3b,c) features much smaller particles of ca. 40 nm in 7 diameter and a CI:Eu intensity ratio close to unity, as expected from a pure oxychloride 8 phase. In both cases, no considerable change in crystal size is observed between the as 9 prepared and equilibrated materials. Finally, CeO₂ evidences even smaller nanoparticles of 10 10-20 nm (as prepared: 5-10 nm) in diameter and exhibits only a minor chlorine peak in the 11 EDX spectrum (Fig. 3d, inset), consistent with the low intensity of this element in the 12 corresponding map and the preservation of the oxide phase evidenced by XRD. To detect 13 possible differences in the surface and bulk composition, XPS analysis was conducted for the as-prepared Eu_2O_3 -p-973, which evidences a Eu 4*d* core level band structure composed 14 of the Eu $4d_{3/2}$ and Eu $4d_{5/2}$ peaks, characteristic of Eu₂O₃ (Fig. 4a) [29,30]. Upon use in 15 ethylene oxychlorination, both of these peaks were shifted to higher binding energy by 2 eV, 16 17 pointing to the presence of neighboring atoms of high electronegativity [29]. A signal detected in the survey spectrum at 198.5 eV [31] in the Cl 2p region unequivocally confirmed 18 the presence of chlorine at the surface (Fig. 4b). In fact, the surface atomic concentrations 19 of Eu, O, and Cl were determined to be 33, 36, and 30%, respectively, which is close to the 20 stoichiometry of the oxychloride phase. 21

Overall, these results demonstrate that ethylene oxychlorination over the lanthanide compounds studied is essentially catalyzed by the oxychloride or chloride phase, including in the case of CeO₂ in which chloride species exist at the surface. However, there are no detectable structural differences between EuOCl and EuOCl-p-973 that would explain their disparity in selectivity. As on CeO₂ the suppression of combustion and the formation of VCM were linked to moderated oxidative properties (catalyzing ethylene oxychlorination to EDC) and the presence of acid sites (needed for EDC dehydrochlorination to VCM [32]), the properties of EuOCl-p-973 and CeO₂ were investigated by H₂-TPR and NH₃-TPD. PrOCl was also studied as a moderately active and unselective reference.

The H₂-TPR profile of CeO₂ (Fig. 5a) shows two H₂ consumption peaks at 761 and 4 5 1090 K, which are attributed to the reduction of labile surface or near-surface oxygen 6 species and the bulk, respectively [32,34]. This very much resembles the analysis of the as-7 prepared CeO_2 samples [22] and indicates that the reducibility of this oxide is not significantly altered under reaction conditions. Pr₄O₇ displays a H₂ consumption peak 8 9 centered at 978 K, however, no H₂ consumption is observed for its analogue PrOCI, 10 indicating that the oxychloride is irreducible in this temperature range. This explains the 11 negligible yields of VCM and CO, observed over this catalyst, which are comparable to the inactive materials. Eu₂O₃-p-973 evidences a broad H₂ consumption peak in the range of 882-12 13 1197 K, while EuOCI-p-973 shows H₂ consumption at significantly higher temperature (similar trend for Eu₂O₃ and EuOCI). Thus, the diminished reducibility of europium 14 oxychlorides compared to CeO₂ is responsible for the lower activity and most importantly the 15 suppression of combustion. However, it is still sufficient to catalyze the formation of EDC. 16

17 NH₃-TPD analyses confirmed that the equilibrated CeO₂ and EuOCl-p-973 catalysts both exhibit significant NH₃ desorption in the range of 525-775 K (Fig. 5b), evidencing the 18 presence of acid sites. This is in line with previous studies on CeO₂ after treatment under 19 chlorination conditions [13,35]. The lower acidity of EuOCI with respect to EuOCI-p-973 is 20 also in accordance with the lower VCM selectivity of the former. Surprisingly, PrOCI shows 21 the highest amount of acid sites by far, which causes the complete transformation of any 22 EDC produced to VCM. Quantification of the amount of ammonia evolved from the two 23 materials with highest VCM yields reveals a significantly higher acid site density in EuOCI-p-24 973 (1.92 μ mol g⁻¹) than CeO₂ (1.45 μ mol g⁻¹), explaining the enhanced VCM formation over 25 the former. 26

1 3.3. Influence of operating conditions

In view of the unprecedented selectivity of EuOCI-p-973, the impact of reaction conditions 2 (namely temperature, HCl and O₂ feed contents, and contact time) on the conversion and 3 product distribution was studied (Fig. 6). These results are compared with CeO₂ calcined at 4 5 1173 K (CeO₂-1173), which was previously reported in ethylene oxychlorination [13]. Both 6 catalysts exhibit an increased conversion with temperature (Fig. 6a), but the enhancement is 7 lower over EuOCI-p-973 than CeO₂-1173. Accordingly, the apparent activation energy 8 (determined from Arrhenius plots, **Fig. S3**) is slightly higher for CeO₂-1173 (28 kJ mol⁻¹) than 9 for EuOCI-p-973 (17 kJ mol⁻¹). Considering the product distribution, the selectivity to VCM 10 increases with reaction temperature over both catalysts, which correlates with a parallel 11 decrease in the EDC selectivity. No CO_x formation is evidenced over EuOCl-p-973 up to 773 K at which point a minor amount of CO is observed, whereas CeO₂-1173 suffers from 12 13 over-oxidation above 673 K, leading to ca. 50% selectivity to CO_x (at 50% C_2H_4 conversion) at 773 K. However, in this comparison of the effect of temperature on the selectivity patterns 14 of the catalysts, the conversion levels differ due to the stronger activity dependence on 15 temperature of CeO₂ than that of EuOCI. Therefore, to decouple the effect of temperature 16 17 and conversion, the latter was raised by changing the space time at 723 K over both catalysts (Fig. 6d). Upon increasing the C₂H₄ conversion over EuOCl-p-973, the selectivity 18 to VCM strongly increases and, reaching 100% at 25% conversion. The selectivity to EDC 19 decreases in equal order, which is consistent with the successive transformation of ethylene 20 to EDC and its dehydrochlorination to VCM. A qualitatively similar decrease of EDC 21 selectivity is also observed over CeO₂-1173 at comparable conversion levels. Nonetheless, 22 the formation of combustion (CO_x) and over-chlorinated (1,2-DCE) products is enhanced 23 instead of VCM. 24

Varying the feed composition also highlights significant differences in the behavior of the two catalysts. Neither the conversion nor the product distribution is significantly affected by the HCl or O_2 feed contents within the investigated range (*i.e.* zero order with respect to HCl

1 and O₂) over EuOCI-p-973. In contrast, CeO₂-1173 exhibits a positive linear activity trend with the HCI feed content and a second order dependency with respect to oxygen 2 (Fig. 6b,c). Furthermore, the EDC selectivity increases with the HCl content in the feed over 3 4 CeO_2 -1173, compensated by decreased CO_x formation. This is expected as a higher degree 5 of chlorination lowers the oxidative strength of the CeO_2 -1173 surface [13,22] and provides more available sites for chlorination. The inverse argument applies for raising the oxygen 6 7 content, which favors combustion and lowers the selectivity to EDC linearly by decreasing 8 the degree of surface chlorination [22]. Combining these results with the insights gained from 9 the bulk and surface characterization, important differences between the two materials can 10 be pointed out. Although CeO₂-1173 preserves the bulk structure of the oxide, the reaction 11 environment alters the nature of the surface from a more oxide- to a more chloride-12 dominated structure, which have different oxidative properties. In contrast, once formed the 13 surface structure of EuOCI-p-973 remains unaltered by the feed conditions. Thus, a change in reaction atmosphere only affects the thermodynamic equilibria, but not the nature of redox 14 sites. 15

To further understand the selectivity patterns of catalysts in ethylene oxychlorination, the 16 17 reaction was split into the four possible processes that can impact the VCM formation. These include the oxidation of C_2H_4 to CO_x , CO to CO_2 , and HCl to Cl_2 , as well as the 18 dehydrochlorination of EDC to VCM (Fig. 7). Each reaction was performed over equilibrated 19 samples: CeO₂ (exhibiting the highest activity), EuOCI-p-973 (attaining the highest VCM 20 yield), and PrOCI (representative of samples exhibiting low activity and high CO formation). 21 In C₂H₄ and HCl oxidation reactions, CeO₂ is the most active material, especially at higher 22 temperatures (Fig. 7a,b), which correlates with its higher reducibility (vide supra, Fig. 5a). 23 24 PrOCI also shows activity for the oxidation of C_2H_4 and CO, with similar or lower light-off temperatures compared to CeO₂, respectively. Note that no CO₂ was generated on PrOCI 25 during ethylene oxychlorination, while in separate oxidation experiments it converted both 26 C₂H₄ and CO to CO₂. XRD analysis revealed that the PrOCI phase partially decomposes and 27

1 re-transforms to the Pr₄O₇ phase during oxidation reactions in the absence of HCI, which is again reducible (Figs. 5a, S4a,b) and thus causes the formation of CO_x. The limited yield of 2 chlorinated products formed on PrOCI (Fig. 1) is explained by its inability to release chlorine 3 4 as seen from its negligible activity in HCI oxidation tests (Fig. 7c). In stark contrast to the 5 above-mentioned systems, EuOCI-p-973 is essentially inactive for the C₂H₄ and CO oxidation reactions (Fig. 7a,b), preserves the EuOCI phase under oxidizing conditions 6 7 (Fig. S4), and has moderate ability to transfer chlorine as evidenced by its mild HCI 8 oxidation activity above 673 K (Fig. 7c). Thus, it appears that the stability of the oxychloride 9 phase and the ability to release chlorine from the surface are key to suppressing the formation of undesired oxidation products and to chlorinate ethylene. 10

11 Finally, the dehydrochlorination of EDC to VCM, was investigated by feeding 1.5 vol.% EDC without or with addition of 3 vol.% O₂ and 4.8 vol.% HCl to the feed (Fig. 7d). The EDC 12 13 concentration was selected to simulate a 50% ethylene conversion to EDC. Furthermore, since CeO₂ was known to yield a 90% conversion to VCM in mixed EDC:O₂:HCl feeds [13], 14 a high EDC feed concentration was preferred to provide improved sensitivity to differences in 15 the performance. Dehydrochlorination activity was observed in all cases. This differed from 16 17 our previous study, in which CeO₂ was found to be inactive in a pure EDC feed. The latter finding can be explained by the fact that in the present study, we evaluated the 18 dehydrochlorination performance on catalysts equilibrated in ethylene oxychlorination, which 19 increased the acidity of these samples. Albeit demonstrating a limited selectivity to 20 chlorinated products in ethylene oxychlorination, PrOCI displays the best EDC 21 dehydrochlorination performance, with or without cofeeding oxygen and HCI, which can be 22 linked to the highest density of acid sites evidenced in this material. However, the inferior 23 24 performance of PrOCI in ethylene oxychlorination can be related to the low tendency of this catalyst to release chloride and it negligible reducibility (vide supra). CeO₂ demonstrates a 25 linear dehydrochlorination trend with temperature when only EDC is fed, while an increased 26 VCM yield and a shift to lower temperatures is attained when O₂ and HCl are mixed with the 27

EDC. Nevertheless, at 773 K the yield is heavily decreased due to more extensive CO formation, which can be traced back to the higher reducibility of CeO_2 (**Figs. 5a, 7a,b**) that causes the combustion of chlorinated products. EuOCl-p-973 exhibits a linear trend with no CO_x formation and an enhanced selectivity to VCM when HCl+O₂ is added to the feed.

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3.4. Integration of high activity and selectivity functions

7 The fact that the VCM yield over EuOCI is limited by its low intrinsic oxychlorination 8 activity while the VCM selectivity over CeO_2 is compromised by the formation of CO_x and 9 over-chlorinated compounds, encouraged us to consider the possibility of integrating the advantageous qualities of each of these rare-earth compounds in the form of mixed oxides. 10 11 Consequently, we prepared samples with molar fractions of europium ranging from 0.3-0.9 by coprecipitation (Table 2). The resulting materials were evaluated in ethylene 12 13 oxychlorination at 673 K to maximize the activity while minimizing the likelihood of overoxidation (Fig. 8). The yield of chlorinated products (and thus the C_2H_4 conversion) is found 14 to reach a maximum over Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773. A further increase in cerium contents in 15 these precipitated samples cause a drop in activity and also lead to the formation of over-16 17 chlorinated products (1,2-DCE).

Analysis by N₂ sorption indicated that the total surface area of the mixed oxides was 18 generally lower than the corresponding single phases (Table 2), which gives a first hint of 19 the interaction of Eu and Ce in these systems. Due to the similar crystal structures of Eu₂O₃ 20 and CeO₂, it is difficult to conclude whether the fresh Eu_xCe_{1-x}O_{2-0.5x}-cp- T_{cal} materials are 21 physical mixtures of the single oxides or atomically-dispersed mixed metal oxides (i.e. 22 having metal to metal interactions/bonding within the oxide network) by XRD (Fig. S5). 23 Analysis of the equilibrated samples only evidences the presence of the EuOCI phase in 24 samples with a europium fraction above 0.6. The fact that the oxychloride is not observed for 25 $x \le 0.5$ corroborates the strong interaction between Eu and Ce in the mixed phase. 26 Consistently, the cell parameter of 5.38 Å was derived for Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773, the best 27

sample in terms of VCM yield, which lies between that of the CeO₂-p-773 (5.35 Å) and 1 Eu₂O₃-p-773 (5.41 Å). Examination by electron microscopy (Fig. 3e) shows that the 2 equilibrated sample is composed of small nanoparticles of ca. 5-10 nm, preserving the 3 crystallinity of the as prepared material (not shown for brevity). The elemental map reveals a 4 5 very homogeneous distribution of europium and cerium atoms, which is also similar to the 6 fresh analogue. Interestingly, the EDX spectrum evidences a small amount of chlorine in the equilibrated sample, which is also corroborated by XPS results showing a shift of the 7 Eu $4d_{3/2}$ and Eu $4d_{5/2}$ peaks to higher binding energy compared to the as-prepared sample 8 due to the presence of chlorine (Fig. 4b). Thus, the oxychloride phase could still exist at the 9 10 surface leading to high acidity. This reasoning is consistent with the highest VCM yield of this sample (Fig. 1). Comparing the performance of Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773 with EuOCI-p-973 11 12 and CeO₂-p-773, it is clear that the mixed oxide leads to very selective VCM formation 13 (Fig. 8) and minimal combustion.

14 Since stability is a crucial driver in the hunt for new catalytic systems to improve the current ethylene oxychlorination process, the long-term performance of EuOCI-p-973 and 15 Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773 was evaluated, demonstrating a stable operation in ethylene 16 17 oxychlorination for over 100 and 40 h on stream with VCM yields of 15% and 19%, respectively (Fig. 9). Even though a minor amount of 1,2-DCE (estimated by carbon mass 18 balance error of about 5-6%) is observed for Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773 up to 20 h, after which it 19 drops with time-on-stream, the mixed oxide evidences higher activity as it is operated at 20 50 K lower temperature and one fourth of the space time (63 g h mol⁻¹ compared to 21 252 g h mol⁻¹). To further assess the stability of EuOCI, we conducted a catalytic test 22 doubling the reactant concentration, which resulted in a very similar selectivity pattern (4% 23 EDC, 96% VCM) as observed under standard conditions at comparable C₂H₄ conversion 24 (19%). Besides, no volatilization of the active phase was evidenced, for example by deposits 25 commonly observed on the reactor walls when using unstable materials, under either 26 condition. Still, the VCM yield achieved is not yet optimal (Fig. 8). In fact, although CeO₂-p-27

1 773 suffers from CO_x and 1,2-DCE formation, the overall yield of desired EDC and VCM was
 2 higher compared to Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773.

3 As an alternative approach to improve the VCM yield, CeO₂ and EuOCI were united in a dual-bed reactor, combining the high activity of CeO₂ in a first bed in the direction of flow in 4 5 order to enhance the EDC formation with the unique selectivity to VCM of EuOCI due to its acidity in a second bed (CeO₂-p-EuOCI-p-db). Advantageously, this could also enable an 6 7 efficient utilization of the heat generated by the exothermic oxychlorination in the 8 downstream endothermic dehydrochlorination. This system indeed results in the highest 9 VCM (27%) and VCM+EDC (33%) yields observed so far at the standard space time of 63 g h mol⁻¹ applied in this study. Even though small amounts of side products (CO₂ and 10 11 1,2-DCE) are formed in the first bed by CeO_2 (Fig. 8), this dual-bed system shows the highest rate of VCM production per unit surface area of the catalyst (Table 2). Since both, 12 13 EuOCI (Fig. 9) and CeO₂ [13] are individually stable, a highly robust operation of this dualbed reactor can be anticipated. 14

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16 4. Conclusions

In this study, we developed a fundamental understanding of the ethylene oxychlorination 17 18 chemistry on scarcely studied rare-earth compounds. Through the integration of steady-state catalytic tests and advanced characterization, we identified EuOCI as the best catalyst for 19 direct VCM production, leading to 96% selectivity and no CO_x formation at 20% ethylene 20 conversion for over 100 h on stream. The consecutive conversion of ethylene to EDC and 21 22 EDC to VCM confirmed the bifunctional reaction mechanism over this catalyst. This unique 23 behavior was found to originate from the transformation of the initial Eu_2O_3 phase to a stable oxychloride. The latter was completely inert towards ethylene and CO oxidation, which 24 explains the absence of undesired CO_x , while it exhibited moderate HCl oxidation, 25 demonstrating its ability to chlorinate ethylene. Other lanthanide oxides, except CeO₂ which 26 retained the oxide structure after reaction, also transformed to their respective oxychloride or 27

1 chloride phases. However, these oxychlorides were either essentially inactive in ethylene 2 oxychlorination or decomposed in oxidative conditions and catalyzed undesired oxidations 3 forming significant amounts of CO_x , as demonstrated for the case of PrOCI. Another crucial 4 aspect of the EuOCI phase was the presence of a high concentration of acid sites, which 5 catalyzed the EDC dehydrochlorination to produce VCM. By combining CeO₂ for its high activity towards EDC with Eu₂O₃ or EuOCI for VCM, in the form of homogeneously mixed 6 7 oxides or as a dual-bed system, respectively, we demonstrated industrially attractive VCM 8 yields (ca. 30%). The intensification feasibility studied herein can be anticipated to be more 9 economical than the current two-step process as it enables reduction of the unit operations 10 eliminating the need for the intermediate EDC purification and subsequent cracking steps.

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Table 1. Total surface area of the samples prior to (fresh) and after (equilibrated) ethylene
oxychlorination. The nomenclature of the used samples reflects the main crystallographic
phase identified in the catalyst.

Fresh sample ^a	S _{BET} ^b (m ² g ⁻¹)	Equilibrated sample	S _{ВЕТ} ^ь (m ² g ⁻¹)
La ₂ O ₃	6	LaCl ₃	8
CeO ₂	45	CeO ₂	28
Pr ₄ O ₇	5	PrOCI	6
Nd_2O_3	32	NdCl₃	21
Sm_2O_3	10	SmOCI	8
Eu_2O_3	11	EuOCI	8
Eu ₂ O ₃ -p-773	37	EuOCI-p-773	26
Eu ₂ O ₃ -p-973	31	EuOCI-p-973	23
Eu ₂ O ₃ -p-1173	14	EuOCI-p-1173	12
Gd_2O_3	5	GdOCI	16
Tb_2O_3	4	TbOCI	7
Dy_2O_3	29	DyOCI	25
Ho_2O_3	7	HoOCI	6
Er_2O_3	60	ErCl ₃	15

^a All samples were commercial, except Eu_2O_3 -p- T_{cal} , which was obtained by precipitation and calcination at T_{cal} K. ^b BET method.

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Sample	Eu:Ceª (mol mol⁻¹)	S _{BET} ^b (m ² g ^{−1})	<i>r</i> (VCM) ^c (mol h ⁻¹ m ⁻²)
Eu ₂ O ₃ -p-973	1:0	31	8.96 x 10⁻ ⁶
Eu _{0.9} Ce _{0.1} O _{1.55} -cp-773	0.9:0.1	16	9.25 x 10 ^{−6}
Eu _{0.5} Ce _{0.5} O _{1.75} -cp-773	0.51:0.49	13	2.24 x 10⁻⁵
Eu _{0.4} Ce _{0.6} O _{1.8} -cp-773	0.39:0.61	27	2.36 x 10⁻⁵
Eu _{0.3} Ce _{0.7} O _{1.85} -cp-773	0.3:0.7	25	1.07 x 10⁻⁵
CeO ₂ -p-773	0:1	44	1.41 x 10 ⁻⁵
CeO ₂ -p-EuOCI-p-db	0.4:0.6 ^d	39 ^d	2.49 x 10 ⁻⁵

Table 2. Characterization data and rate of VCM formation of the mixed europium-cerium
oxides.

^a XRF. ^b BET method. ^c Corresponds to data in **Fig. 8**. ^d Estimated.



2 Scheme 1. Scheme of the laboratory set-up used for the catalytic studies. 1: on-off valves, 3 2: mass flow controllers, 3: mixer, 4: vaporizer, 5: syringe pump, 6: quartz reactor, 7: oven, 8: catalyst bed, 9: heat tracing, 10: three-way bypass valve, 11: NaOH scrubber, 4 PI: pressure indicator, and TI: temperature indicator. The three positions at which the 5 6 temperature was measured in the catalyst bed are indicated on the left, lying within ±1 K 7 (measured in a reference experiment over CeO₂-1173 at 31% C₂H₄ conversion). The inset 8 on the right depicts a representative chromatogram where the peaks are assigned to the 9 following compounds: o,■ Ar and CO (due to the overlapping retention time, these peaks were subsequently separated by mass spectrometry), \diamond C₂H₄, \checkmark CO₂, \star vinyl chloride, 10 • 1,2-cis-dichloroethene, and \blacktriangle ethylene dichloride. 11



2 Fig. 1. Product yields (Y) in ethylene oxychlorination over single metal lanthanide catalysts.

3 The inset depicts the Arrhenius plot of VCM formation over CeO₂, EuOCI, and EuOCI-p-973.

4 Conditions: T = 723 K, C_2H_4 :HCI: O_2 :Ar:He = 3:4.8:3:3:86.2, $W_{cat}/n^0(C_2H_4) = 63$ g h mol⁻¹.

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Fig. 2. XRD patterns of selected catalysts prior to (black) and after (red) ethylene oxychlorination. Vertical lines beneath the diffractograms and structures on the right denote identified crystalline phases according to the ICDD PDF numbers provided on the left of the figure. The gray rectangles in the structures represent the corresponding unit cells. Dashed boxes in the diffractogram of LaCl₃ highlight the reflections for LaOCl·H₂O (ICDD PDF 70-2139). XRD analysis of all other investigated lanthanide-based catalysts is depicted in **Fig. S2**.

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2 Fig. 4. a) Eu 4d and b) Cl 2p core level XPS spectra of fresh (black) and equilibrated (red)

3	europium-based	catalysts.
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- 2 Fig. 5. a) H₂-TPR and b) NH₃-TPD profiles of selected fresh (dashed lines) and equilibrated
- 3 (solid lines) catalysts.



Fig. 6. C_2H_4 conversion and product selectivity over EuOCI-p-973 (left) and CeO₂-1173 (right) as a function of **a**) *T* at fixed HCI (4.8 vol.%) and O₂ (3 vol.%) concentrations, **b**) feed HCI content at fixed O₂ content (3 vol.%) at 723 K (EuOCI) and 673 K (CeO₂), and **c**) feed O₂ content at fixed HCI content (4.8 vol.%) at 723 K (EuOCI) and 673 K (CeO₂). **d**) Selectivity to

products *versus* conversion at different space times at 723 K at fixed HCl (4.8 vol.%) and O₂ (3 vol.%) concentrations, color code as in **a-c**. Conditions: **a-c**) $W_{cat}/\dot{n}^0(C_2H_4) = 63$ g h mol⁻¹, **d**) $W_{cat}/\dot{n}^0(C_2H_4) = 6-252$ g h mol⁻¹.

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2 Fig. 7. Performance descriptors for selective VCM production over equilibrated catalysts. a) C_2H_4 oxidation to CO_2 ($C_2H_4:O_2:Ar:He = 3:3:3:91$, $W_{cat}/n^0(C_2H_4) = 63 \text{ g h mol}^{-1}$), **b**) CO 3 oxidation to CO₂ (CO:O₂:Ar:He = 2.5:2.5:3:92, $W_{cat}/\dot{n}^{0}(CO) = 76 \text{ g h mol}^{-1}$), **c**) HCl oxidation 4 $W_{\rm cat}/\dot{n}^0$ (HCl) = 63 g h mol⁻¹), CI_2 $(HCI:O_2:Ar:He = 3:3:3:91,$ d) EDC 5 to and dehydrochlorination to VCM. In **d**) $W_{cat}/\dot{n}^{0}(EDC) = 126 \text{ g h mol}^{-1}$, open symbols: EDC: 6 Ar:He = 1.5:3:95.5, and solid symbols: EDC:HCI:O₂:Ar:He = 1.5:4.8:3:3:87.7. 7

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Fig. 8. Product yields in ethylene oxychlorination over EuOCl-p-973, CeO₂-p-773, mixed oxides of Eu and Ce, and the dual-bed configuration of CeO₂-p-773 and EuOCl-p-973. Conditions: T = 673 K, C₂H₄:HCl:O₂:Ar:He = 3:4.8:3:3:86.2, W_{cat}/\dot{n}^0 (C₂H₄) = 63 g h mol⁻¹.



Fig. 9. C_2H_4 conversion and product selectivities *versus* time-on-stream in ethylene oxychlorination over **a**) EuOCl-p-973 and **b**) Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773. Conditions: T = 723 K (673 K for Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773), C₂H₄:HCl:O₂:Ar:He = 3:4.8:1.5:3:87.7 (C₂H₄:HCl:O₂:Ar:He = 3:4.8:3:3:86.2 for Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773), W_{cat}/n^0 (C₂H₄) = 252 g h mol⁻¹ (63 g h mol⁻¹ for Eu_{0.4}Ce_{0.6}O_{1.8}-cp-773).

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8	Supplementary Material
9	Lanthanide compounds as catalysts for the one-step synthesis of vinyl chloride from ethylene
10	Matthias Scharfe, [†] Pedro A. Lira-Parada, [†] -Amol P. Amrute, Sharon Mitchell, and Javier Pérez-Ramírez*
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Fig. S1. X-ray fluorescence spectra of commercial lanthanide oxides. Vertical lines show the reference positions of the
 respective lanthanide. The excellent match of the reference line with the measured spectra confirms the high purity of
 the samples.



Fig. S2. X-ray diffraction patterns of the samples prior to (black) and after (red) the oxychlorination of ethylene.
Vertical lines beneath the diffractograms and structures on the right denote identified crystalline phases according to
the ICDD PDF numbers provided on the left of the figure. The gray rectangles in the structures represent the

- 1 corresponding unit cells. Dashed boxes in the diffractogram of LaCl₃ indicate the reflections for LaOCl·H₂O (ICDD
- 2 PDF 70-2139). All oxides matched the supplier specification except Pr_2O_3 , which showed the reflections of Pr_4O_7 .



4 Fig. S3. The Arrhenius plot of C₂H₄ conversion in ethylene oxychlorination over EuOCl-p-973 and CeO₂-1173.

5 Conditions: C_2H_4 :HCl: O_2 :Ar:He = 3:4.8:3:3:86.2, $W_{cat}/\dot{n}^0(C_2H_4) = 63$ g h mol⁻¹.



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Fig. S4. X-ray diffraction patterns of EuOCl, PrOCl, and CeO₂ a) after C₂H₄ oxidation and b) after CO oxidation.
Vertical lines show the phases identified in the samples: red (CeO₂), green (Pr₄O₇), blue (PrOCl), and black (EuOCl).
ICDD PDF numbers are provided on the left of the figure. Dashed boxes in PrOCl diffractograms show the Pr₄O₇
phase that is formed from PrOCl upon oxidation of C₂H₄/CO.



Fig. S5. X-ray diffraction patterns of mixed europium-cerium oxides prior to (black) and after (red) the oxychlorination
of ethylene. Vertical lines denote the crystalline phases identified in the solids: red (CeO₂), gray (EuOCl), and blue
(Eu₂O₃). ICDD PDF numbers are provided on the left of the figure.