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Olefins from Natural Gas via Oxychlorination Catalysis

Guido Zichittella, Nicolas Aellen, Vladimir Paunović, Amol P. Amrute, and Javier Pérez-Ramírez*

Abstract: Ethylene and propylene are the key building blocks of the chemical industry, but current processes are unable to close the growing gap between demand and manufacture. Herein, we report an exceptional europium oxychloride (EuOCl) catalyst for the selective (≥95%) production of light olefins from ethane and propane *via* oxychlorination chemistry, achieving yields of ethylene (90%) and propylene (40%) unparalleled by any existing olefin production technology. The outstanding performance was rationalized by its bifunctional character, integrating the alkane oxychlorination into alkyl chloride and its dehydrochlorination into the olefin, thus recycling the halogen source. Moreover, EuOCl is able to process mixtures of methane, ethane, and propane to produce the olefins, thereby reducing separation costs of the alkanes in natural gas. Finally, the EuOCl catalyst was scaled up in technical form, which preserves the outstanding performance for >150 h under realistic process conditions.

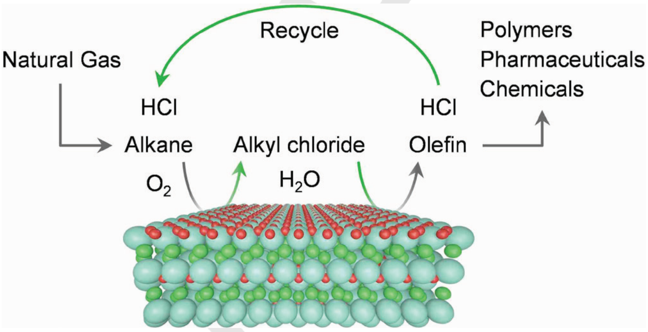

Figure 1. Closed-loop chlorine-mediated process for the one-step conversion of abundant light alkanes to valuable ethylene and propylene, which are the main building blocks of the chemical industry. An optimal catalytic material for this process should integrate the ability to functionalize the alkane into the corresponding alkyl chloride and to dehydrochlorinate the latter to yield an olefin, enabling the full recycle of the halogen source.

Vast conventional and unconventional natural gas reserves are rich in ethane and propane, offering a great potential as feedstock to produce ethylene and propylene, the platform molecules for the manufacture of virtually all polymers, pharmaceuticals, and chemicals.[1] Currently, these olefins are produced *via* steam-cracking, fluid-catalytic cracking, and/or catalytic dehydrogenation, which are highly capital- and energy-intensive and are unable to close the growing gap between their demand and manufacture.[1b,2] Thus, the replacement of these highly endothermic technologies with one-step, exothermic processes would result in enormous economic benefits.[2c,3] In this direction, the oxidative dehydrogenation of ethane and propane,[2a,4a] the partial oxidation of ethane,[4b,c] and the oxidative coupling of methane[4d] have been extensively studied for decades as a way to attain olefins, but so far they have failed to reach commercial reality due to the lack of suitable catalysts that can achieve economically attractive yields of ethylene and propylene (<75% and 30%, respectively). The catalytic alkane oxychlorination route, comprising the reaction of an alkane with hydrogen chloride (HCl) and oxygen, is appealing as it enables to selectively functionalize the alkane under moderate conditions.[1a,5] However, so far this route has mainly targeted the production of vinyl chloride monomer or alkyl chloride, where ethylene or propylene was observed as a by-product with low yields of 50% or 20%, respectively.[1a,6] The selective production of ethylene and propylene in a single step from the corresponding alkane would be highly appealing. This requires the design of a multifunctional catalytic material that can integrate the oxychlorination of the alkane to the alkyl chloride, followed by its dehydrochlorination to yield the olefin (**Figure 1**).

In our quest for a novel multifunctional catalytic active phase, we have investigated the gas-phase oxychlorination of ethane and propane under variable conditions over different catalytic families, including: cerium oxide (CeO_2), vanadyl pyrophosphate ($(VO)_2P_2O_7$), titanium oxide (TiO_2), iron phosphate ($FePO_4$), and europium oxychloride (EuOCl). The oxide and phosphate systems were selected based on their good activity in methane oxyhalogenation,[5b,7a] while the choice of EuOCl was based on the recent studies revealing its promising performance for ethylene oxychlorination to vinyl chloride monomer,[7b] and of europium oxybromide for methane oxybromination to methyl bromide and HBr oxidation to Br_2.[7c] The catalysts were compared by evaluating the product distribution obtained in the oxychlorination of ethane and propane at *ca.* 20% and 15% alkane conversion, respectively (**Figure 2a**,**b**; Supporting Information, **Figure S1**), obtained by adjusting the reaction temperature. Based on this criterion, the catalysts can be classified into three different groups. The first category is represented by CeO_2, which led to the lowest yields of olefin due to the formation of chlorinated hydrocarbons and combustion products in EOC and particularly POC. The second class, represented by $(VO)_2P_2O_7$ and TiO_2, achieved high yields of ethylene (with 80% and 90% selectivity in EOC, respectively), however, caused pronounced formation of combustion products in POC. Finally, $FePO_4$ and EuOCl enabled to reach over 95% selectivity to alkene in both EOC and POC. EuOCl displayed the highest yields of ethylene and propylene at unaltered selectivity (*vide infra* **Figure 3c**; Supporting Information, **Figure S4**), thus emerging as an outstanding catalyst for olefin production *via* oxychlorination chemistry. X-ray diffraction (XRD) and N_2 sorption analyses of all materials before and after the catalytic tests showed no alterations of the crystallographic structure, but evidenced a small decrease in the total surface area (Supporting Information, **Figure S2**). We have assessed the stability of this promising active phase, and demonstrated its robustness in

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[*] G. Zichittella, N. Aellen, V. Paunović, Dr. A. P. Amrute,
Prof. J. Pérez-Ramírez
Institute for Chemical and Bioengineering
Department of Chemistry and Applied Biosciences, ETH Zurich
Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland
E-mail: jpr@chem.ethz.ch

Supporting information for this article is given via a link at the end of the document.

preserving the outstanding performance for over 100 h on stream in both EOC and POC (Supporting Information, **Figure S3**). The XRD analysis of the samples collected after the run indicated no alternation of the bulk structure (Supporting Information, **Figure S3**) while a slight increase in the crystallinity of the sample was evidenced from high resolution transmission electron microscopy (HRTEM) and by a small drop in the total surface area (Supporting Information, **Figure S3**). We sampled the materials after 5 h on stream in both EOC and POC and confirmed that the surface area (8 m^2 g^{-1} in both cases) stabilizes after few hours on stream. Thermodynamic calculations show that the transformation of EuOCl to $EuCl_3$ is highly disfavored in the operating conditions of the oxychlorination reaction (Supporting Information, **Figure S3**), which might be due to its structural arrangement, alternating halide and oxide layers, as shown in **Figure 1**. Finally, we have conducted elemental analysis on the used catalyst and confirmed the absence of coke deposits (Supporting Information, **Table S4**).

Further evaluation of EuOCl under variable conditions showed the preservation of high selectivity (>90%) in a wide range of temperatures (623-847 K), and feed concentration of alkanes (1.5-6 vol.%), O_2 (3-6 vol.%), and HCl (1-15 vol.%) (**Figure 2c**,**d**), highlighting the robustness of EuOCl in both reactions. The formation of alkenes might in principle come from the oxidative dehydrogenation of the alkane over the catalyst. Thus, to demonstrate the pivotal role HCl in the feed in alkane activation and olefin generation, a test was performed in the absence of HCl. Both the alkane conversions and alkene selectivities were drastically dropped (**Figure 2c**,**d**). Interestingly, by switching from 0 vol.% to 1 vol.% of HCl, the alkane conversion and particularly olefin selectivity were boosted in both alkane oxychlorination reactions. Further optimization of the alkane inlet concentrations enabled the attainment of the highest single-pass yields of ethylene and propylene (90% and 40%, respectively) among any alkane-to-olefins upgrading route (**Figure 2c**,**d**).

Olefin production from alkane *via* oxychlorination chemistry stem from the integration of alkane oxychlorination to produce alkyl chloride and subsequent dehydrochlorination of the latter to to yield the corresponding alkene on the catalyst surface (*vide supra* **Figure 1**). Nonetheless, these chloro-derivatives were not

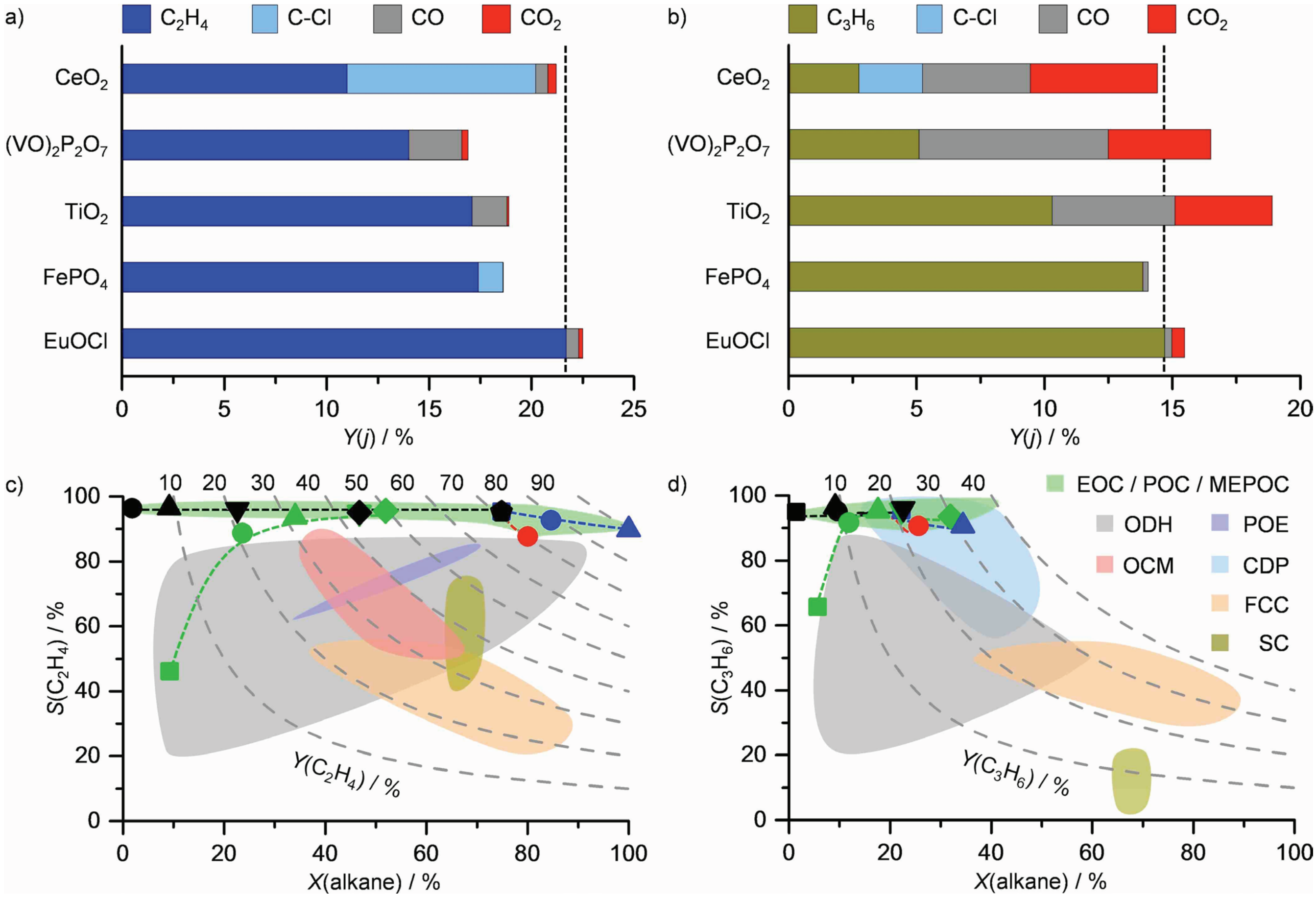

Figure 2. Catalytic performance expressed as single-pass yield of products (*Y*(*j*)) in the oxychlorination of a) ethane (EOC) and b) propane (POC) at *ca.* 20% and 15% alkane conversion, respectively, and alkene selectivity *versus* alkane conversion over EuOCl in c) EOC and d) POC at variable conditions. EuOCl represents a superior catalyst for both reactions, leading to the highest yield of olefins (dashed lines in a) and b)). Conditions: Alkane:HCl:O_2:Ar:He = 6:6:3:4.5:80.5. *GHSV* = 2550-6950 h^{-1} (details in Supporting Information, **Table S3**). EuOCl was further studied in c) EOC and d) POC at variable temperature (black) and feed concentration of HCl (green), O_2 (red), and alkane (blue) (details of symbols in Supporting Information, **Table S2**). *GHSV* = 6370 h^{-1}. The dashed gray lines indicate the olefin yield, whereas the colored areas denote the alkane conversion and olefin selectivity achievable in the oxychlorination of light alkanes and their mixtures over EuOCl (EOC, POC, MEPOC; green; *vide infra* Supporting Information, **Figure S5**), oxidative dehydrogenation of ethane and propane (ODH; gray),[2a,4a] partial oxidation of ethane (POE; blue),[4b,c] oxidative coupling of methane (OCM; red),[4d] catalytic dehydrogenation of propane (CDP; light blue),[1b] fluid catalytic cracking (FCC; orange)[8a] and steam cracking (SC; yellow)[8b] of ethane and naphtha. All results are expressed on a molar basis.

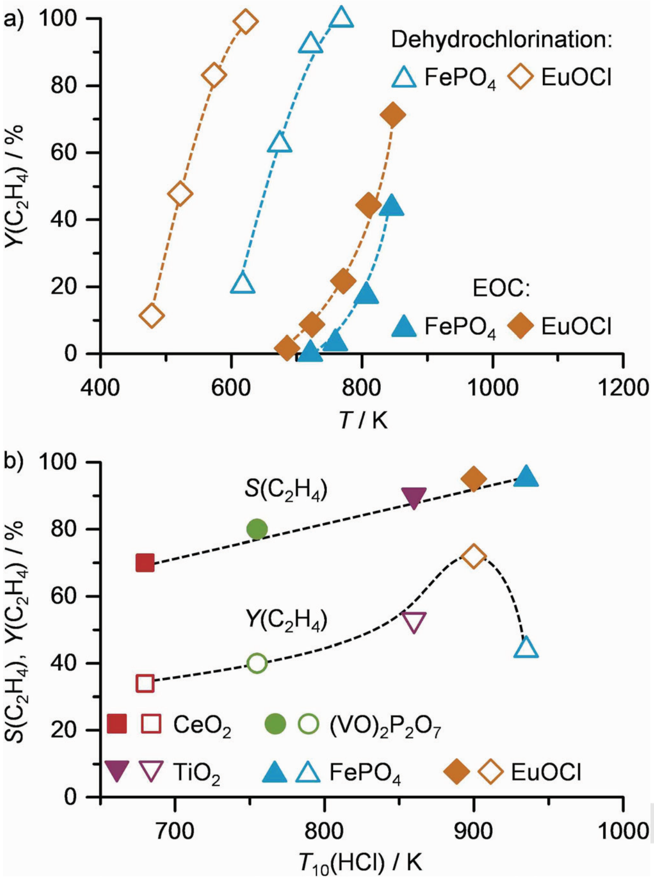

Figure 3. a) Yields of ethylene *versus* temperature in C_2H_5Cl dehydrochlorination (open symbols) and in EOC (solid symbols) over EuOCl (orange) and $FePO_4$ (blue). Conditions: *GHSV* = 3570-6370 h^{-1} (details in Supporting Information, **Table S3**). C_2H_5Cl dehydrochlorination: C_2H_5Cl:Ar:He = 1:4.5:94.5, EOC: C_2H_6:HCl:O_2:Ar:He = 6:6:3:4.5:80.5. b) Selectivity (solid symbols) and yield (open symbols) of ethylene in EOC *versus* the oxidizing ability of the catalyst under typical oxychlorination conditions (T_{10}(HCl)). The latter is measured as the temperature to attain 10% HCl conversion in the gas-phase HCl oxidation to Cl_2 (Supporting Information, **Figure S4**). Conditions: C_2H_6:HCl:O_2:Ar:He = 6:6:3:4.5:80.5. *GHSV* = 2550-6950 h^{-1} (details in Supporting Information, **Table S3**).

observed over EuOCl (*vide supra* **Figure 2a**,**b**; Supporting Information, **Figure S1**), which might be explained by its fast dehydrochlorination kinetic. To confirm this, we performed ethyl chloride and propyl chloride dehydrochlorination experiments on EuOCl and $FePO_4$ and observed that ethylene and propylene generation occurred at much lower temperature compared to EOC and POC, particularly in the case of EuOCl (**Figure 3a**; Supporting Information, **Figure S4**).

To rationalize the different performance of the catalysts in EOC and POC, the gas-phase HCl oxidation to Cl_2 was studied (Supporting Information, **Figure S4**) and taken as a relative measure of the oxidizing ability of the catalysts under typical oxychlorination conditions. Thus, if the temperature at which *ca.* 10% HCl conversion is attained in HCl oxidation, T_{10}(HCl), is high, the material possesses a low oxidizing character. This temperature was found to correlate linearly with olefin selectivity in EOC and POC (**Figure 3b**; Supporting Information, **Figure S4**), suggesting that the systems with lower reducibility are preferred to achieve a high olefin selectivity, as a likely consequence of the suppressed combustion reactions as evidenced in the case of EuOCl and $FePO_4$ (*vide supra* **Figure 2a**,**b**). However, if the reducibility is too low, the olefin yield will be low as seen for $FePO_4$. EuOCl appeared to have the optimal oxidizing potential, as it achieves the highest yields of olefins in both EOC and POC (**Figure 3b**; Supporting Information, **Figure S4**). Thus, the outstanding performance of EuOCl can be rationalized by its balanced redox properties, enabling it to selectively functionalize the alkane and suppress undesired reactions, and its unpaired ability to readily dehydrochlorinate the produced alkyl chloride, allowing it to selectively yield olefins and to recycle the halogen source (Supporting Information, **Figure S5**.

Due to the increasing scarceness of oil reserves, the world is currently undergoing an unprecedented revolution in raw hydrocarbons feedstock supply, with vast natural gas being the leading flag.[9] Consequently, we explored the potential of EuOCl in the oxychlorination of mixtures of methane, ethane, and propane (MEPOC) (Supporting Information, **Figure S5**) to show the level of flexibility of this catalytic technology with respect to the feed composition. In this reaction, the onset temperature for propylene formation was lower than the one for ethylene, in line with the higher activity observed in POC than EOC. At 773 K, 20% and 27% yield of ethylene and propylene were achieved at >95% selectivity (Supporting Information, **Figure S5**). Methane conversion and CO_x formation were negligible (<5%). Moreover, we have investigated the effect of increased feed concentration of HCl and varying reactants ratio on the catalytic performance (Supporting Information, **Figure S5**), which show that the yields of ethylene and propylene could be improved to 30% and 40%, respectively, at >95% selectivity. In this respect, the olefins mixture could then potentially be upgraded by known technologies to gasoline blends over zeolite- or supported metal-based systems.[10] These results show an attractive feature of the EuOCl catalyst preserving the high alkene selectivity in the alkane mixture, which gives an extra-potential for natural gas upgrading due to its low sensitivity to feed purity.

To demonstrate the practical potential of EuOCl-based system for olefin production, we developed a technical catalyst by dispersing europium (10 wt.%) onto millimeter-sized bodies of silicon carbide (SiC), silicon oxide (SiO_2), zirconium oxide (ZrO_2), and titanium oxide anatase (TiO_2-a). Evaluation of these systems in EOC and POC identified EuOCl/TiO_2-a as the best catalyst for ethylene production, enabling unaltered ethylene selectivity and higher ethane conversion compared to bulk EuOCl, and EuOCl/SiC as the best system for propylene production, maintaining >90% propylene selectivity and reaching 40% propylene yield (Supporting Information, **Figure S6**). This suggests that the carrier selection plays an important role in controlling the performance of the EuOCl phase. We performed XRD analysis of the best ethylene and propylene generators before and after the catalytic tests (**Figure 4a**,**b**, Supporting Information, **Figure S7**). No europium phases were identified over EuOCl/TiO_2-a, indicating its high dispersion. On the other hand, reflections of Eu_2O_3 phase could be distinguished in the equilibrated EuOCl/SiC sample, suggesting (*i*) lower europium dispersion, and (*ii*) likely strong active phase-support electronic interactions that inhibits the transformation of Eu_2O_3 into EuOCl over SiC. Transmission electron microscopy (TEM) in high-angle annular dark field mode (HAADF) and high resolution TEM corroborated the high and low europium dispersion in the

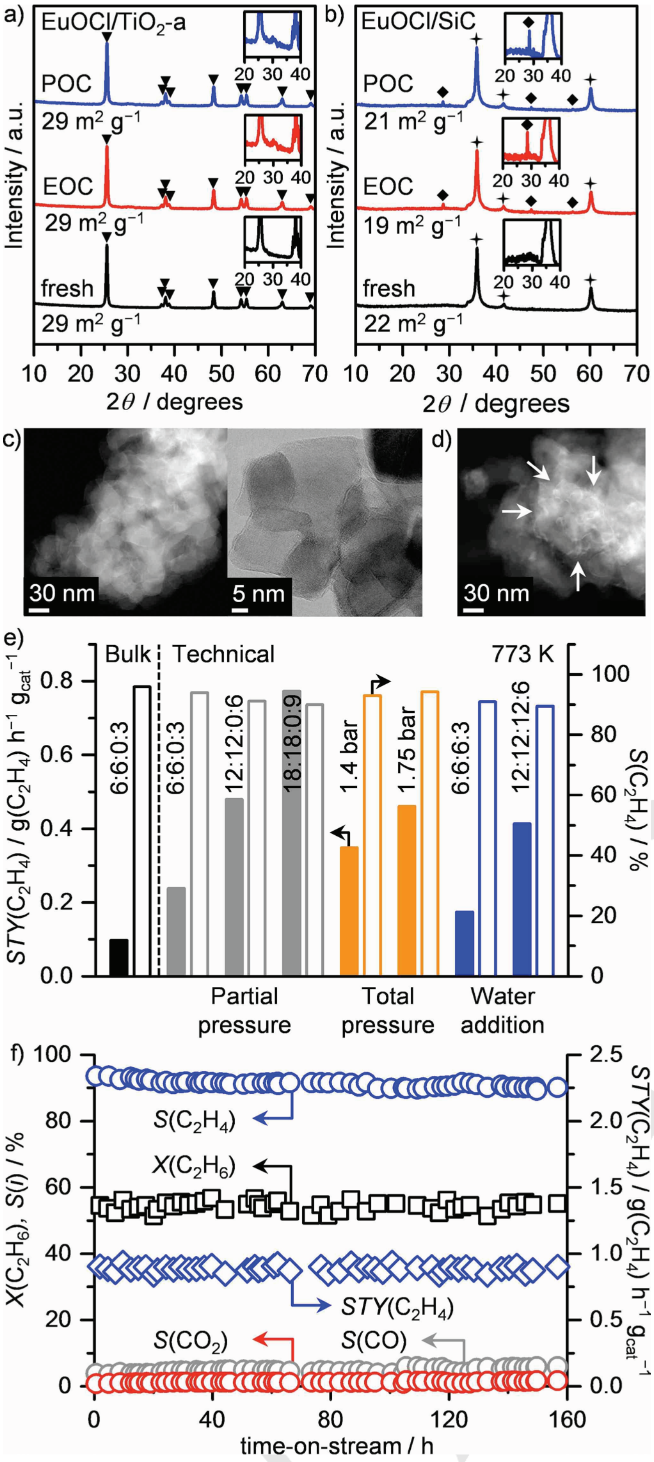

Figure 4. X-ray diffractograms and total surface area of a) EuOCl/TiO$_2$-a and b) EuOCl/SiC prior to (fresh) and after EOC and POC. The insets magnify the diffractograms in the region of 20°-40° 2θ. Marked reflections according to the JCPDS reference patterns: TiO$_2$-anatase (triangle), SiC (star), Eu$_2$O$_3$ (diamond). c) Transmission electron microscopy (TEM) in high-angle annular dark field mode (HAADF), and high resolution TEM of used EuOCl/TiO$_2$-a, and d) HAADF-TEM of used EuOCl/SiC. e) Ethylene space time yield (*STY*(C$_2$H$_4$); solid bars) and ethylene selectivity (open bars) in EOC at increasing reactants concentration (gray) and total pressure (orange), and in the presence of water (blue). The numbers in the sample code denote the molar feed ratio (C$_2$H$_6$:HCl:H$_2$O:O$_2$). f) Alkane conversion, product selectivity and ethylene space time yield *versus* time-on-stream over EuOCl/TiO$_2$-a extrudates in the oxychlorination of ethane. Conditions: W_{cat} = 0.5 g, *GHSV* = 8080 h^{-1}, C$_2$H$_6$:HCl:H$_2$O:O$_2$:Ar:He = 12:12:12:6:4.5:65.5.

EuOCl/TiO$_2$-a and EuOCl/SiC catalysts, respectively (**Figure 4c**,**d**, Supporting Information, **Figure S8**).

Further evidence on the importance of the carrier selection comes from the alkane oxidation, and the alkyl chloride dehydrochlorination (in the presence or absence of oxygen) tests conducted over these catalysts (Supporting Information, **Figure S9** and **10**). It was found that EuOCl/TiO$_2$-a possesses low tendency towards alkane combustion, and high activity in the dehydrochlorination of C$_2$H$_5$Cl, making it a very effective catalyst for ethylene production. On the other hand, it fails in POC due to its high reactivity in combusting C$_3$H$_7$Cl. EuOCl/SiC, instead, is more inert towards C$_3$H$_7$Cl oxidation. This together with its low tendency to combust the alkane, and its good activity in dehydrochlorination makes it a much better catalyst for POC.

To further demonstrate the practical relevance of the presented catalytic technology, the best ethylene producer, EuOCl/TiO$_2$-a extrudates, was taken as representative, analyzed in greater details and evaluated under more demanding conditions. Microscopy measurements by scanning TEM in HAADF mode with elemental mapping by energy-dispersive X-ray (EDX) spectroscopy showed the regularity of the surface as well as uniform distribution of europium along the extrudate before and after the reaction (Supporting Information, **Figure S11**). Mercury porosimetry showed the preservation of the meso- and macroporosity of the extrudate (Supporting Information, **Figure S12**). X-ray photoelectron spectroscopy of the samples evidenced the presence of Eu^{2+} on the catalytic surface, which slightly increases after being exposed to the reaction environment (Supporting Information, **Figure S12**), suggesting the Eu^{3+}/Eu^{2+} to be the active redox couple, in line with other studies on Eu-based catalysis.[7c]

To verify the robustness of shaped EuOCl/TiO$_2$-a, we have studied the effect of higher reactants partial pressure and total pressure over this catalyst in EOC. A three-fold increase in the concentration of reactants led to a more than three times higher ethylene space time yield at ≥90% selectivity. Likewise, upon increasing the total pressure from atmospheric until 1.75 bar, a two-fold increment of *STY*(C$_2$H$_4$) was achieved at >90% selectivity (**Figure 4e**). Carbon elemental analysis (Supporting Information, **Table S4**) of the sample recovered after 5 h exposure to three times higher reactant concentration demonstrated the absence of coke. Moreover, we have tested EuOCl/TiO$_2$-a by using N$_2$ as the carrier gas instead of He and observed that the catalytic performance was preserved.

Although today mature technologies for HCl/H$_2$O separation are applied in industry,[11a,b] effective and tailored methods would be required to separate water since it is a net reaction product. In this view, we have studied the effect of stoichiometric water addition to EOC feed over EuOCl/TiO$_2$-a. Ethylene selectivity of ≥90% was attained despite a small drop in productivity, which could be partially restored by doubling all reactants partial pressures (**Figure 4e**), demonstrating that an operation with dry HCl is not critical to maintain the outstanding performance. Finally, we have evaluated EuOCl/TiO$_2$-a extrudates in a long-term test at higher reactants partial pressure and by water co-feeding, which showed its ability to retain the outstanding performance for over 150 h and its mechanical, surface, and bulk physicochemical properties (**Figure 4f**; Supporting Information, **Figure S12**).

In conclusion, we have discovered EuOCl as a highly promising catalytic technology for the selective one-step conversion of ethane and propane into olefins *via* oxychlorination chemistry, providing the highest single-pass yields of ethylene and propylene (90% and 40%, respectively) among any existing technology for olefin production. The performance of EuOCl was rationalized by (*i*) its balanced redox properties that allows to functionalize the alkane and to avoid combustion, and by (*ii*) its unpaired ability to dehydrochlorinate the formed alkyl chloride to olefin, enabling the recycling of the halogen source. Moreover, EuOCl is also able to selectively process mixtures of methane, ethane, and propane to produce ethylene and propylene. Finally, we demonstrated the scalability of the EuOCl-based catalyst in extrudate form using widely available carriers. Titanium oxide anatase was identified as the best support for ethylene production, which maintained the outstanding performance for over 150 h on stream at both increased reactants partial pressure and by co-feeding water. These results show the practical relevance of the EuOCl-based chemistry for natural gas upgrading, and drives future research on several macroscopic engineering aspects, such as heat management, products separation (*i.e.* H_2O, HCl, CO_x), reactor design *etc.*, for further demonstration of the applicability of this highly promising catalytic technology, although relevant solutions can be extrapolated from applied technologies.[11]

Experimental Section

Details on the catalyst preparation, characterization, and evaluation are provided as Supporting Information.

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Keywords: europium oxychloride • halogen chemistry • heterogeneous catalysis • light olefins • natural gas upgrading

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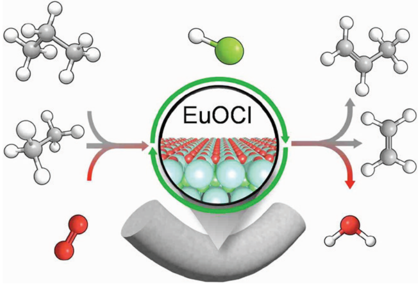
Entry for the Table of Contents

COMMUNICATION

Gas to olefins: Ethylene and propylene can be generated from ethane, propane, or mixtures of methane, ethane, and propane over europium oxychloride *via* oxychlorination chemistry at yields surpassing any existing technology for alkene production. Its performance can be preserved in technical form, testifying the practical relevance of this catalytic technology for olefin production.



*Guido Zichittella, Nicolas Aellen, Vladimir Paunović, Amol P. Amrute, and Javier Pérez-Ramírez**

Page No. – Page No.
Olefins from Natural Gas via Oxychlorination Catalysis