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Review

Ceria in halogen chemistry

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ABSTRACT

Halogen chemistry constitutes an essential part in the industrial production of polymers and gains increasing attention as an attractive strategy to activate light alkanes that constitute natural gas. CeO₂-based catalysts offer an exciting potential for advances in hydrogen halide recovery that enables a high efficiency of halogen-based processes for activation of small molecules. This review provides an overview of recently developed ceria-based catalysts in the context of polymer industry (polyvinyl chloride, polyurethanes, and polycarbonates) and activation of light hydrocarbons for natural gas upgrading. In addition, mechanistic insight and the challenges of ceria catalysts are provided, aiding the design of future catalytic materials and applications.

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1. Introduction

Cerium is the most abundant rare earth element, which is widely used in catalysis in the oxide form CeO₂ (ceria) [1]. Apart from its most prominent application in three-way catalysts (TWC) for exhaust gas treatment, interest in ceria as catalyst for other processes, such as the water gas-shift reaction, water splitting, steam reforming, or as component in photocatalysis of fuel cells, increased strongly in recent years [1,2]. A key aspect for the suitability of ceria in these reactions is its characteristic of providing oxygen storage capacity due to the ability of Ce to alternate between Ce³⁺ and Ce⁴⁺ states [2]. Another field where such abilities can be of use is halogen chemistry, in which oxidation or oxychlorination processes are of significant practical interest. Still, works discussing applications of CeO₂ in these fields did not tackle this material as primary

focus or were limited to review its use only in the oxidation of halogenated volatile organic compounds [3,4]. Considering that materials such as polyvinyl chloride (PVC), polyurethanes (PU), and polycarbonates (PC) account for 57% of the overall chlorine production (75 Mton per year) [5,6], chlorine mediated functionalization or chlorine-containing products are an essential part of many industrial sectors [5]. In particular, chlorine production through catalytic HCl oxidation (Deacon reaction) dates back to the 1870s and the so-called balanced vinyl chloride (VCM) process, involving ethylene chlorination, thermal dehydrochlorination, and HCl recycling through ethylene oxychlorination has been industrially practiced since the 1950s, rendering chlorine chemistry well-established industrial processes [6–8]. These processes and with them the related catalytic materials, which are generally based on the chlorides of copper, have been greatly optimized during the past decades.

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Fig. 1. Scheme depicting the four areas of ceria-catalyzed halogen chemistry described in this review.

Nonetheless, the inherent instability of cupric chloride systems under harsh reactions conditions remains one of the persisting challenges in the application of these technologies, yet extensive changes in the original catalyst formulation or disruptive decisions to opt for radical new routes are rarely made [5,9]. Similarly, natural gas upgrading to chemicals and fuels started in the 1920s by methane chlorination, after which many additional processes such as the corresponding oxychlorination, halogenation of higher alkanes, halogen-mediated alkane de-

hydrogenation, coupling of methyl halides (CH_3X) to higher hydrocarbons, pyrolysis of methyl halides to chemicals, and alkane oxyhalogenation were developed [6]. Recently halogen chemistry saw a revival due to the development of new catalysts, featuring unprecedented stability and selectivity. This review aims at providing a brief overview of the promising catalytic potential of ceria in halogen chemistry, and in particular will discuss its use in the field of hydrogen halide oxidation, C_2H_4 oxychlorination, and oxyhalogenation of methane and higher alkanes (Fig. 1), finally outlining possible directions for future developments and industrial applications.

2. Halogen chemistry in polymer industry

2.1. HCl oxidation

The manufacture of several polymers, in particular polyvinyl chloride (PVC), polyurethanes (PU), and polycarbonates (PC) releases HCl as by-product (Fig. 2a), which has been typically recycled *via* oxychlorination in the context of the balanced VCM process (Fig. 2a, left). Nonetheless, as the PU and PC de-

Fig. 2. (a) Simplified schemes of processes for the production of polyvinyl chloride and polyurethanes, highlighting ethylene oxychlorination and HCl oxidation for HCl recycling. (b) Conversion (X_{HCl}) in HCl oxidation over the representative catalysts, adapted with permission from ref. [6]. (c) Reaction profile for HCl oxidation on $\text{CeO}_2(111)$, where the initial state exhibits one oxygen vacancy, and (d) XRD patterns of ceria samples in fresh form and after use at various O_2/HCl ratios, adapted with permission from ref. [14]. (e) Space-time yield (STY) of HCl oxidation as a function of the Cl:Ce ratio in *operando* PGAA measurements, evidencing the dynamic and reversible nature of CeO_2 under chlorinating conditions in HCl oxidation, adapted with permission from ref. [15]. The inset on the right depicts the working principle of *operando* PGAA.

mand surpasses the one of PVC, additional HCl recycling to Cl_2 from these processes (exemplified by PU synthesis in Fig. 2a, right) or other by-product HCl from the chemical industry becomes highly necessary. Even though technological advances in recent years significantly lowered the power consumption of electrochemical routes [5,6], catalyzed HCl oxidation remains the most energy efficient technology [6]. After many decades of improving the catalyst stability of the original copper-based catalysts that were originally devised in 1870, several hurdles still hampered the industrial application into today's times. These included (i) low single pass HCl conversion, (ii) loss of activity due to active phase volatilization, (iii) environmental concerns regarding alternative chromium-based materials, and (iv) corrosion issues due to unreacted HCl in presence of product H_2O [5,10,11].

The last decade testified a significant progress in the fundamental understanding of the Deacon reaction, which led to the development of stable HCl oxidation catalysts that could overcome the above listed challenges (Fig. 2b). Herein, RuO_2 -based materials represent the leading active phase due to their high activity at low temperatures and structural stability that is enabled by the confinement of chlorination to the uppermost layers [12,13]. However, the relatively high and often fluctuating price of ruthenium prompted the development of alternative catalytic systems [6]. In 2012, Amrute *et al.* [6] first uncovered the high performance of bulk CeO_2 in HCl oxidation. In-depth theoretical studies put forward the mechanism of this reaction, which involves the Cl activation in an oxygen vacancy ($\square$), followed by its transition on top of a Ce atom (*) and recombination with a neighboring Cl^* , finally leading to desorption of molecular Cl_2 . The transition step is the rate determining step, and requires 2.15 eV (Fig. 2c). The hampered chlorine evolution is responsible for the enhanced surface chlorination at stoichiometric or sub-stoichiometric O_2 :HCl ratios (≤ 0.25). Notably, although energetically hindered by 3 eV, progressive subsurface chlorination still occurs at very low O_2 :HCl ratios due to vacancy diffusion [14]. This is evidenced by the appearance of reflections attributed to CeCl_3 species in the XRD patterns of catalysts exposed to feed mixtures with low O_2 :HCl ratios, while exposition to oxygen rich feeds, with O_2 :HCl ≥ 0.75 (standard conditions: O_2 :HCl = 2) fully preserves the CeO_2 phase in the used catalyst (highlighted boxes in Fig. 2d) [14]. Additional insights into the chlorination behavior of CeO_2 under different reaction conditions were acquired by *operando* measurements of the chlorine content of bulk CeO_2 during HCl oxidation using prompt-gamma activation analysis (PGAA), a non-destructive technique that exploits a beam of cold neutrons to excite atomic nuclei, which upon relaxation emit element-characteristic gamma rays. PGAA showed that chlorination of ceria is reversible, and correspondingly restoration of the activity in HCl oxidation is possible by modification of the O_2 :HCl feed ratios (Fig. 2e) [15]. In particular, low O_2 :HCl initially decreased the activity and increased the degree of chlorination, while a following increase to O_2 :HCl = 2 increased the activity due to the positive dependence of the reaction on the O_2 feed content, yet failed to fully remove the chlorine species in the catalyst [14,15]. At O_2 :HCl = 9, full activity was regained,

leaving only subsurface chlorination, irrelevant for activity [15]. In order to further improve the performance of ceria, investigations of Hf or Zr doped ceria indeed revealed increased activity of the resulting catalysts, while trivalent dopants were found to be detrimental [16,17]. Other strategies, such as supporting ceria on a variety of carriers, revealed the activity order: $\text{CeO}_2/\text{ZrO}_2 > \text{CeO}_2/\text{Al}_2\text{O}_3 \geq \text{CeO}_2/\text{TiO}_2$ (Fig. 3a), in line with results of CeO_2 - ZrO_2 mixed oxides [18]. While the activity increased linearly with the Ce loading on Al_2O_3 , $\text{CeO}_2/\text{ZrO}_2$ did not show an increase of activity above a Ce content of 7–10 wt.% (Fig. 3a) [19]. The outstanding performance of $\text{CeO}_2/\text{ZrO}_2$ was attributed to the presence of CeO_2 nanostructures, evidenced by H_2 -TPR and electron microscopy, ranging from clusters to nanoparticles with strong interaction or even intermixing of the ceria phase with the support, while $\text{CeO}_2/\text{Al}_2\text{O}_3$ and $\text{CeO}_2/\text{TiO}_2$ showed defined nanoparticles with sizes of 3–15 nm and 20–50 nm, respectively (Fig. 3b). Considering the link between activity and degree of chlorination, evidenced for bulk ceria (*vide supra*), *operando* PGAA was used to evaluate the different chlorine uptake of $\text{CeO}_2/\text{ZrO}_2$ and $\text{CeO}_2/\text{Al}_2\text{O}_3$ (Fig. 3c). Therein $\text{CeO}_2/\text{ZrO}_2$ exhibited lower chlorination compared to $\text{CeO}_2/\text{Al}_2\text{O}_3$ over the whole investigated range of conditions, in accordance with the higher activity of the former, further corroborating the importance of chlorination. Therefore, $\text{CeO}_2/\text{ZrO}_2$ rendered as suitable candidate for upscaling, tested in form of shaped catalyst bodies in a pilot plant and showing stable HCl conversion over 700 h on stream (Fig. 3d). This goes in a new paragraph of the reaction, leading to possible hot-spot formation in the catalyst bed, results in a high probability for RuO_2 to form volatile RuO_4 species under oxidative conditions. Therefore, complex cascade reactor schemes with intermittent cooling and HCl side feeds are necessary for ruthenium-based systems (Fig. 3e). However, one option to better utilize the heat of reaction and allow operation at temperatures higher than 663 K, is to combine the ruthenium-based catalyst with $\text{CeO}_2/\text{ZrO}_2$, which requires higher temperature (Fig. 2b), but also exhibits improved stability under such conditions (Fig. 3d), in staged dual-catalyst bed reactors for adiabatic operation, as shown in Fig. 3e [20,21]. Therein the first bed of RuO_2 -based material generates the heat necessary for HCl oxidation over $\text{CeO}_2/\text{ZrO}_2$. This strategy reduced the number of unit operations by half, while preserving the same productivity, which significantly reduces capital and catalyst cost [6].

2.2. Ethylene oxychlorination for vinyl chloride manufacture

Vinyl chloride (VCM), the monomer of the third most produced plastic polyvinyl chloride, is produced through hydrochlorination of acetylene or through energy-intensive thermal dehydrochlorination of ethylenedichloride (EDC) with a low yield of 49%–58%. EDC is, in turn, formed either by Cl_2 addition to ethylene or by ethylene oxychlorination. The latter enables recycling of HCl from the dehydrochlorination step in the balanced VCM process (Fig. 2a). To date, the catalyst in ethylene oxychlorination comprises cupric chloride (CuCl_2) as the active phase, impregnated on a porous support such as alumina, and is promoted by numerous alkali, alkaline-earth, and rare-earth

Fig. 3. (a) STY of HCl oxidation as a function of the Ce content in supported CeO₂ catalysts, (b) micrographs of supported CeO₂ catalysts, (c) STY in HCl oxidation as a function of the Cl:Ce ratio in *operando* PGAA measurements, and (d) Stability evaluation of shaped CeO₂/ZrO₂ pellets (3 mm diameter) in HCl oxidation, as adapted with permission from ref. [19]. (e) Temperature (top) and HCl conversion (bottom) as a function of the axial coordinate of an adiabatic reactor cascade, containing either single RuO₂/TiO₂ beds (left), or staged RuO₂/TiO₂ and CeO₂/ZrO₂ beds. Catalyst or reactor temperature limits, as well the equilibrium conversion, are indicated by dashed lines. The left and right panels are adapted with permission from ref. [6].

metals to reduce the copper loss and/or improve the activity and selectivity (Fig. 4a). However, while an EDC selectivity of 99% is achieved, issues surrounding active phase volatilization due to hot-spot formation in fixed-bed reactors, or particle stickiness in fluidized-bed reactors have not yet been fully resolved (Fig. 4a) [22]. Alternative catalysts, such as palladium or rhodium-based materials showed reasonable initial activities and selectivities to VCM. Nonetheless their stability remains unknown. In contrast, LaOCl was reported to exhibit a high VCM selectivity but low activity [23–25], which limits its potential for large-scale implementation [6]. Recently, CeO₂ was identified as highly active catalyst, in a screening of representative HCl oxidation catalysts in ethylene oxychlorination, in addition showing direct VCM formation with high yield (Fig. 2b) [9]. In comparison to the copper-based catalyst, 200 K higher temperature was necessary to reach the same conversion levels for IrO₂ and RuO₂, which showed mainly CO_x formation, attributed to their strong redox properties, while CeO₂ exhibited three times higher activity and minimal CO_x selectivity. This was attributed to moderated redox properties, while still preserving the ability to activate HCl [9]. In addition, CeO₂ exhibited no structural (Fig. 4c), or morphological changes, and preserved stable performance during ethylene oxychlorination at typical reaction conditions [9]. Optimization of reaction con-

ditions (Fig. 4d) showed that increased temperature or contact time are beneficial for VCM selectivity but in parallel increase formation of unwanted 1,2-dichloroethene (DCE). This selectivity dependence on the contact time hinted a consecutive mechanism of VCM formation through EDC dehydrochlorination, which is corroborated by separate tests of the latter, leading to VCM promoted by the presence of HCl in the feed [9]. On the other hand, HCl rich feeds suppressed CO_x and enhanced EDC formation, leaving the VCM selectivity unaltered [9,22]. Tuning the surface area of bulk ceria, which also affected the acidity, or engineering of CeO₂-ZrO₂ mixed oxides resulted in up to 25% VCM yield, higher than any previously reported system, which was attributed to enhanced acid properties of the materials, which promote dehydrochlorination of *in-situ* formed EDC to VCM [9]. However, these catalysts also promoted the formation of unwanted by-products (DCE, CO_x) [9], and the detailed reaction mechanism remained unknown.

Therefore, detailed mechanistic studies, involving a combination of density functional theory (DFT), steady-state experiments, and temporal analysis of products (TAP) were performed [22], revealing that in ethylene oxychlorination, the catalyst surface contains CeOCl, while the bulk phase remains or evolves to CeO₂, regardless of the starting materials CeCl₃, CeOCl, or CeO₂ [22]. In addition, the CeO₂(111) surface was

Fig. 4. (a) Schematic illustration of the state-of-the-art catalyst used in fluidized-bed reactors and concepts of related particle stickiness or active phase volatilization due to hot-spot formation usually found in fixed-bed reactors. (b) Ethylene conversion ($X_{C_2H_4}$) and product selectivity (S_j) over Cu-K-La-Cl_x/Al₂O₃ at 473 K, and IrO₂, RuO₂, and CeO₂ at 673 K, and (c) XRD patterns of Cu-K-La-Cl_x/Al₂O₃ and CeO₂ samples in the fresh and used form, as adapted with permission from ref. [9]. The crystalline phases identified in the CuCl₂-based sample change strongly upon reaction. The symbols ●, □, ▽, and ◆ denote reflections attributed to γ-Al₂O₃ (JCPDS 48-0367), Cu₂(OH)₃Cl (JCPDS 70-0821), CuCl₂·2H₂O (JCPDS 71-2288), and KCl·CuCl₂ (JCPDS 20-0874), respectively. (d) Ethylene conversion ($X_{C_2H_4}$) and product selectivity (S_j) as a function of temperature (left) and selectivity (S_j) as a function of conversion ($X_{C_2H_4}$, right) in ethylene oxychlorination over ceria, as adapted with permission from ref. [22].

found more active than the (100) surface due to stronger chlorination of the latter, while the selectivity patterns rendered comparable [22]. Nevertheless, concentrating on the more relevant, lowest energy (111) surface, the degree of oxygen removal from CeO₂, realized by H₂ pretreatment, and the replenishment of the accordingly formed oxygen vacancies by Cl, led to decreased activity, increased selectivity to chlorinated products and decreased selectivity to carbon oxides (Fig. 5a). Furthermore, the complex ethylene oxychlorination network (Fig. 5b) was modeled by DFT on a defect CeO₂(111) surface with an empty or chlorinated vacancy, which revealed that the most likely pathway of VCM formation takes indeed place by a cascade reaction (Fig. 5c). First, EDC appears and then HCl is extracted in a concerted step to lead to VCM, where the latter concerted steps are a key characteristic of ceria. This concerted step lowers the energy barrier by about 1 eV in comparison to individual steps, enabled by the hexagon-like structure formed by the electron density of surface and transition state structure [23]. In addition, this pathway was corroborated by TAP, showing that EDC is the first product in ethylene oxychlorination, followed by VCM (inset in Fig. 5c) [22]. Notably, EDC formation requires a chlorinated vacancy and a Cl adsorbed on a Ce center, while EDC dehydrochlorination can, if EDC does not desorb, continue on the just created vacancy, leaving it chlorin-

ated in the end and available for further ethylene activation. However, DCE formation was found possible from VCM or EDC, once a non-chlorinated vacancy is present, for example after EDC desorption. CO was found to originate from chlorinated species, whereas CO₂ can either stem from further oxidation of CO or directly from ethylene [22]. To overcome these intrinsic limitations, other lanthanide materials were investigated, possibly offering different redox and acid properties that still allow EDC formation and dehydrochlorination to VCM, while hindering creation of empty vacancies that might lead to unwanted products [26]. *Ex-situ* characterization of the used catalysts revealed that the oxide forms of all compounds, except CeO₂, transformed into their respective (oxy)chloride. While CeO₂ still exhibits the highest activity, europium oxychloride (EuOCl) led to the best vinyl chloride selectivity (Fig. 5d), where calcination temperature (provided in K in the catalyst name) of the oxides prepared by precipitation (indicated by the letter p in the catalyst name) was found to affect the activity, reaching at most half of the one of CeO₂. This performance could be rationalized by the unique balance of mild redox and enhanced acid properties of EuOCl compared to CeO₂ (Fig. 5e), which suppress over-oxidation and boost EDC dehydrochlorination. Strategies to couple the excellent selectivity of EuOCl with the high activity of CeO₂ were demonstrated by synthesis of homogeneous

Fig. 5. (a) Conversion ($X_{C_2H_4}$), selectivity (S_i), and catalyst chlorine content in ethylene oxychlorination over CeO_2 catalysts, (b) reaction network showing the main (solid black) and side pathways, and (c) reaction profile and corresponding optimized structures on a defective $CeO_2(111)$ surface (solid black pathway in (b)) including temporal analysis of products (TAP) as inset, as adapted with permission from ref. [22]. (d) Product yields in ethylene oxychlorination over lanthanide catalysts, and (e) H_2 -TPR (left) and NH_3 -TPD (right) of selected lanthanide catalysts as adapted with permission from ref. [26].

europium-cerium mixed oxides, reaching an optimal ratio of $Eu:Ce = 0.4:0.6$ ($EuCeO_x$ in Fig. 5d), which demonstrates the successful integration of enhanced oxychlorination and dehydrochlorination functions on a single surface [26].

3. Halogen-mediated natural gas upgrading

Natural gas is a highly attractive post-oil resource for the production of valued-added chemicals and liquid fuels owing to

the high content of methane and other light alkanes (ethane, and propane), and large reserves that may last for over a century [6,27]. Nonetheless, the conventional activation of methane *via* steam reforming into syngas and ethane and propane *via* steam cracking into ethylene and propylene requires high temperatures and pressures, which results in energy-intensive processes and costly plants that are only economical at large scale [27]. This, along with the high cost of the natural gas transportation to the centralized facilities using pipelines or in the form of liquefied natural gas, precludes the valorization of 30%–60% of the total reserves that are distant from the market and/or can be extracted at low productivity rates [6,28]. This so-called stranded gas is nowadays often vented or wastefully burnt by flaring, causing over 13 billion USD losses per year and significant environmental concerns [29]. Therefore, novel catalytic processes that could allow for efficient low-temperature activation of alkanes into multipotent petrochemical intermediates are sought after to unlock the valorization of natural gas. Selective functionalization of C–H bonds using halogens, *i.e.*, chlorine and bromine emerged as an attractive strategy to accomplish this goal (Fig. 6) [6,27,30]. In particular, methane can be reacted with molecular halogen (X_2) to form halomethane (CH_3X). This intermediate represents a halogen analogue of methanol and can be transformed into virtually all base chemicals using the catalytic routes that are similar to methanol coupling. In general bromination, provides a higher fraction of CH_3X as compared to chlorination, while CH_3Br and CH_3Cl exhibit similar activity patterns in CH_3X coupling. Nonetheless, the ability to close the halogen loop by completely recycling the hydrogen halide (HX) that is released as a stoichiometric byproduct in both halogenation and coupling steps constitutes the condition *sine qua non* for the commercial success of halogen-mediated alkane upgrading given the much higher price of halogens (particularly bromine) with respect to final products (Fig. 6).

To this end, catalytic HX oxidation with oxygen (or air) into X_2 (Deacon reaction, *vide supra*), and catalytic oxyhalogenation, comprising the activation of alkane with hydrogen halide and oxygen to form alkyl halides or olefins constitute the most promising approaches for sustainable halogen recovery.

Fig. 6. Process-flow diagram of the halogen mediated natural gas upgrading. Adopted with permission from ref. [30].

3.1. HBr oxidation

Catalytic HBr oxidation constitutes the bromine analogue of the well-established Deacon process with much less pronounced thermodynamics constraints [31]. Namely, complete HBr conversion, *i.e.*, full bromine recovery is attainable at temperatures up to *ca.* 750 K in contrast to the HCl oxidation that is equilibrium limited already at *ca.* 450 K. As early as in 1939, the patent filed by Hooker discloses the process for HBr oxidation, which besides the oxides and salts (mostly chlorides) of nickel, cobalt, manganese, copper, and thorium, states the application of supported cerium-based catalysts [32]. Notably, this is the first known report on the use of cerium-containing materials in halogen-related processes. This class of catalysts, and especially cerium oxide, remained in the center of interest of the industrial patents until today, mainly due to their relatively high activity and stability against volatilization [31,33–39]. In particular, the light-off curves of cerium-based catalysts in HBr oxidation are shifted towards *ca.* 50 K higher temperatures as compared to the most active RuO_2 system and fall into the industrially attractive low-temperature window (< 673 K) that enables to avoid the thermodynamically imposed conversion constraints and allows for the use of more affordable corrosion-resistant construction materials (Fig. 7a). Besides, high melting and boiling points of cerium (oxy)bromides that can be formed upon bromination of the starting ceria-based materials prevent catalyst volatilization, which is the most prominent deactivation mechanism of transition metal-based systems in HBr oxidation [31,40]. Nonetheless, similar to RuO_2 , bulk CeO_2 exhibits a high propensity to bromination that is especially pronounced at low reaction temperatures and small oxygen excess in the reaction feed [33,40]. As a consequence, the light-off curve of ceria displays a prominent hysteresis behavior, *i.e.*, a shift toward lower HBr conversions when the temperature is decreased and then increased again over the same temperature range due to a high bromine uptake at low temperatures (Fig. 7a). In addition, ceria experiences a fast activity drop when the inlet feed comprises the (near) stoichiometric molar ratio of reactants ($O_2:HBr = 0.25$, Fig. 7b), which is in turn another relevant process requirement that potentially allows for the use of air as oxidizing agent and eliminates the need for an oxygen plant [40]. The alterations of activity are correlated with the appearance of new phases in the diffractograms of the used catalyst that can be ascribed to cerium bromides (Fig. 7c) [33,40]. A depth-profile analysis indicates a fast build-up of bromides on the catalyst surface followed by progressive marked ceria propensity to bromination. Hereby, the halogen uptake in HBr oxidation is higher as compared to HCl oxidation at identical $O_2:HX$ ratios and comparable reaction rates and has a negative impact on the productivity of bromine evolution (Fig. 7e) [33]. The bromination of CeO_2 causes a Ce^{4+} to Ce^{3+} reduction (Fig. 7d, inset), thus precluding the formation and healing of oxygen vacancies that are essential for its oxidation activity. Hence, it can be inferred that the cerium bromide phases are inactive in HBr oxidation and that the high performance in this reaction necessitates an oxybromide-like surface structure formed over a bulk ceria phase [31,33,40]. Consider-

Fig. 7. HBr conversion (a) over CeO_2 and RuO_2 as a function of temperature (molar ratio $\text{O}_2:\text{HBr} = 2$) and (b) over CeO_2 as function of time on stream ($T = 523 \text{ K}$, $\text{O}_2:\text{HBr} = 0.25$). (c) XRD and (d) XPS analysis of CeO_2 catalysts recovered after various tos in the stability test presented in (b). (e) Rate of halogen production over homogeneous ceria-zirconia catalysts as a function of halogen uptake ($T = 523 \text{ K}$ in HBr oxidation and $T = 698 \text{ K}$ in HCl oxidation, $\text{O}_2:\text{HX} = 0.75$). (f) Space time yield (STY) as a function of tos over homogeneous ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-h}$) and non-homogeneous ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-nh}$) ceria-zirconia catalysts ($T = 523 \text{ K}$, $\text{O}_2:\text{HBr} = 2$). (g) HBr conversion over EuOBr , $\text{EuOBr}/\gamma\text{-Al}_2\text{O}_3$, and TiO_2 -rutile catalysts as a function of temperature ($\text{O}_2:\text{HBr} = 2$). (h) EDX elemental maps and HRTEM micrographs (inset) of $\text{EuOBr}/\gamma\text{-Al}_2\text{O}_3$ catalyst used in HBr oxidation. (i) HBr conversion over $\text{EuOBr}/\gamma\text{-Al}_2\text{O}_3$ ($T = 523 \text{ K}$, $\text{O}_2:\text{HBr} = 0.25$) and TiO_2 -rutile ($T = 823 \text{ K}$, $\text{O}_2:\text{HBr} = 0.275$) catalysts as a function of tos . In (a) and (g) temperature was decreased from the highest to the lowest value (down), and then increased back to the starting point (up). Data in plots (a)–(d) and (g)–(i) adopted with permission from refs. [31,40], and data in plots (e) and (f) were adopted with permission from ref. [33].

ing the positive effect of zirconia on decreasing the energy of vacancy formation of ceria as well as higher resistance of zirconia-supported ceria catalysts against the chlorine uptake in HCl oxidation (*vide supra*), the mixed ceria-zirconia catalysts ($\text{Ce}_y\text{Zr}_{1-y}\text{O}_2$) were put forward as a strategy to enhance the activity and particularly stability of ceria in HBr oxidation [33]. The analysis of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalysts with homogeneous ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-h}$) and non-homogeneous ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-nh}$) metal dispersion revealed the promotional effect of zirconia on the activity of CeO_2 irrespective of the metal homogeneity in the mixed oxide. Nonetheless, the metal distribution has a prominent impact on the bromination propensity of ceria, whereby $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-h}$ catalyst exhibits up to 50% lower bromine uptake as compared to the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-nh}$. Moreover, the increase in Zr fraction further reduces the bromine

content of the used homogeneous catalyst (Fig. 7e). For comparison, the chlorine uptake during HCl oxidation over these materials is much less affected with both the distribution and relative ratios of the metal (Fig. 7e). Since the space-time yield of bromine decreases at higher Zr ratios, the optimum balance between the high bromine productivity and resistance to bromination is attained for Zr contents in the range of 70–90 mol.%. However, in spite of the stability improvement with respect to bulk CeO_2 and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-nh}$ catalysts, $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-h}$ exhibits an activity loss as the bromination of ceria cannot be inhibited to a full extent (Fig. 7f).

These results indicate that the resistance of a catalyst towards extensive bulk bromination constitutes a key descriptor for its stability in HBr oxidation, which is in turn challenging to attain by altering the structure of ceria. To this end, research

has been recently directed towards alternative active phases, comprising lanthanide-based and rutile catalysts. In particular, systematic investigation of a range of lanthanide oxides other than ceria revealed that these materials readily form oxybromide phases when exposed to the HBr oxidation environment, which is a behavior similar to the oxide-oxychloride transformation observed in ethylene oxychlorination [40]. Among various oxybromides, EuOBr displays a unique combination of the inherent stability of the partially brominated phase that is preserved in both oxygen- and HBr-rich feed mixtures and high activity that exceeds that of CeO₂ in the low-temperature range (Fig. 7g), which is related to the redox active Eu³⁺/Eu²⁺ couple. Notably, the activity of EuOBr was further promoted by its supporting over γ -Al₂O₃ carrier that enables near atomic europium dispersion and stabilization of the brominated form of the catalyst (Fig. 7i). Thereby, EuOBr/ γ -Al₂O₃ catalyst prepared in the form of technical extrudates displays a stable performance under practically relevant conditions (Fig. 7j).

Considering a high activity, but limited stability of the RuO₂-rutile catalyst in HBr oxidation, yet another research direction focused on the alternative rutile-type materials in this reaction [41,42]. Hereby, TiO₂-rutile catalyst was identified as an attractive active phase exhibiting a light-off curve that is shifted to *ca.* 100 K higher temperatures with respect to CeO₂, but similar to EuOBr shows no hysteresis effect (Fig. 7g). In addition, the catalyst performance remains stable under operation at near stoichiometric O₂:HBr ratio in the inlet feed (Fig. 7j). The unusual oxidation activity and stability of TiO₂-rutile was ascribed to a self-doping mechanism. Herein, the bromine adsorbed on the catalyst surface generates defect states in the band structure that allow for oxygen activation and confine the bromination to the catalyst surface (halogen coverage is limited up to *ca.* 50%) as the subsurface incorporation of the bromine atoms becomes highly endothermic.

3.2. Oxyhalogenation of alkanes

In oxyhalogenation reactions, the alkane is reacted with HX and O₂ over a catalyst to produce alkyl halide (and/or olefins) and water. Although this route enables 100% halogen atom efficiency in contrast to direct halogenation that is limited to 50%, the use of oxygen poses a significant challenge in terms of overoxidation, leading to the formation of undesired carbon oxides (CO_x) [6]. Still, the different reactivity of halogenated compounds in oxychlorination and oxybromination reactions necessitates the systematic engineering of catalytic materials in the respective chemistries in order to tailor their redox properties, for which lanthanides- and especially cerium-based materials offer great possibilities [6].

To date, research has mainly focused on the oxyhalogenation of methane, the main component of natural gas, reporting a wide range of catalytic materials such as supported precious metals, metal oxides, including CeO₂, and oxyhalides, as well as metal phosphates [6,28,30,43–46]. In particular, the activity in the oxychlorination and oxybromination reactions over these systems was compared to the catalysts' reactivity in the oxidation of HX to molecular halogen, which were quantified based

on the temperature at which 10% conversion of CH₄ in oxyhalogenation, T_{10} CH₄ oxyhalogenation, and of HX in HX oxidation, T_{10} HX oxidation, were achieved, respectively (Fig. 8a) [43]. Interestingly, the catalysts in CH₄ oxybromination lie on the left side of the plot, indicating that the rate of methane consumption is lower than that of Br₂ production over these systems. On the other hand, in CH₄ oxychlorination the catalysts were found across the diagonal of the plot, where CH₄ consumption and Cl₂ production are competing. Furthermore, the activity in CH₄ oxychlorination was found to linearly correlate with the catalysts' ability to evolve molecular halogen, T_{10} HX oxidation (Fig. 8a), which was also preserved over a wide temperature range as corroborated by the linear dependence among the apparent activation energies of CH₄ oxychlorination and HCl oxidation [43]. Contrarily, the activity in CH₄ oxybromination correlated weakly with the catalysts' ability to evolve Br₂ and no dependence between the activation energies of the former reaction and of HBr oxidation was found. This, together with the fact that CH₄ oxyhalogenation occurs in the same temperature window of non-catalytic gas-phase CH₄ halogenation (Fig. 8a), led to the hypothesis that the former reaction proceeds *via* the catalytic oxidation of HX into X₂ and its consecutive reaction with methane in the gas-phase [30,43]. The differences observed were mainly attributed to the proposed distinct rate determining steps, the oxidation of HCl in oxychlorination and the reaction of CH₄ with Br₂ in oxybromination [43]. In order to provide insights into this mechanism, CH₄ oxyhalogenation was investigated over a representative catalyst (Pd/SiO₂) by *operando* photoelectron photoion coincidence (PEPICO) spectroscopy (Fig. 8b and 8c), which enables the detection of reactants, products, and intermediates such as radicals during reaction conditions [45]. Besides detecting the presence of methyl (CH₃[•]), chlorine (Cl[•]), and bromine (Br[•]) radicals, a correlation between the formation of methyl halide (CH₃X) and of CH₃[•] radicals was observed, which was found strong in oxybromination and weaker in oxychlorination (Fig. 8b and 8c). Further analyses revealed that the observed rate in CH₄ oxybromination is primarily ($\geq 90\%$) determined by gas-phase pathways, while in CH₄ oxychlorination gas-phase and surface-driven routes are at least equivalent, which is in agreement with observations gathered from the comparison with HX oxidation (*vide supra*) [43,45].

Despite non-catalytic pathways play a significant role in CH₄ activation in oxyhalogenation, thus leading to the inevitable formation of polyhalomethanes, generation of undesired CO_x was found catalyst-dependent (Fig. 8d and 8e) [43]. By comparing the performance of this material in CH₄ oxychlorination and oxybromination at *ca.* 20% CH₄ conversion, it was observed that the formation of CO_x in oxybromination was found much more severe (selectivity $\approx 50\%$) than in oxychlorination (selectivity $\approx 15\%$) (Fig. 8e). Furthermore, a higher production of dihalomethane (CH₂X₂) was observed in oxychlorination (selectivity $\approx 17\%$) compared to oxybromination (selectivity $\approx 5\%$). In order to rationalize these selectivity patterns, the rate of CH₄ oxyhalogenation was compared with that of CH₄, HX, and CH₂X₂ oxidation over CeO₂ (Fig. 8d) [43]. The rate of HCl oxidation was significantly higher in comparison to the rate

Fig. 8. (a) Temperature required to obtain 10% CH₄ conversion in methane oxyhalogenation, T_{10} CH₄ oxyhalogenation, as a function of the ability of the catalysts to evolve molecular halogen, T_{10} HX oxidation, defined as the temperature needed to obtain 10% HX (X = Cl, Br) conversion in HX oxidation. The green and brown lines denote the temperature at which 10% CH₄ conversion is obtained in the gas-phase chlorination and bromination of methane, respectively. Adapted with permission from refs. [40,43,45,47]. Correlation between the peak areas of methyl halide and methyl radical in methane (b) oxychlorination and (c) oxybromination over Pd/SiO₂ at different conditions as determined by *in situ* photoelectron photoion coincidence spectroscopy. Adapted with permission from ref. [45]. (d) Reaction rates of CH₄ oxyhalogenation and of the oxidation of HX, CH₂X₂, and CH₄ as a function of temperature over CeO₂. Adapted with permission from ref. [43]. (e) Selectivity to product *j* in the oxyhalogenation of (e) methane, (f) ethane, and (g) propane over lanthanides-based systems at *ca.* 20% alkane conversion. C-X refers to the sum of halocarbons with the same carbon number of the reactant, whereas cracking products represent all the hydrocarbons formed with a lower carbon number than the starting alkane. Adapted with permission from refs. [28,40,43,44,48–54].

of oxychlorination, which was in turn greater than the rate of CH₂Cl₂ and CH₄ oxidation. From this activity order, it followed that in oxychlorination the chloromethanes are formed at a higher rate than they are consumed in the corresponding oxidation reactions, in good agreement with the relatively high selectivity to these products. Moreover, since HCl oxidation is significantly faster than CH₂Cl₂ and especially CH₄ oxidation, it may reduce the concentration of O₂ in the sys-

tem, which can additionally suppress the oxidation of the alkane and of chloromethanes. On the other hand, the rate of oxybromination was significantly lower than the rate of CH₂Br₂ oxidation, suggesting that bromomethanes, once produced, readily undergo oxidation, thus resulting in a limited selectivity to these products [43,50]. Nevertheless, the rate of HBr oxidation is still higher than the rate of CH₂Br₂ oxidation, indicating that these two reactions could compete in the consumption of

O₂.

Accordingly, different strategies were devised in order to suppress the undesired formation of CO_x. Firstly, a high content of HX in the feed of oxyhalogenation was used over CeO₂ in order to take advantage of the competition between the partial reactions of HX and CH₂X₂ oxidation within the oxyhalogenation reaction network [43]. Although a small decrease in CO_x production was observed in oxychlorination, going from 15% to 10% selectivity, a much more pronounced inhibition was shown in oxybromination, where CO_x selectivity diminished from 50% to ca. 2% (Fig. 8e). This was attributed to the surface reduction of CeO₂ by halogen adsorption, which is already pronounced and not strongly influenced by HCl addition in oxychlorination, while in oxybromination necessities a high content of HBr in the feed to be comparable to that in oxychlorination due to facile bromine evolution over this catalyst [43]. An alternative strategy is the preparation of solid solutions of CeO₂ and transition metal oxides (MO_x). This was demonstrated by Wang and co-workers, which showed that FeO_x-CeO₂ and NiO-CeO₂ could obtain a combined selectivity to halomethanes (CH₃X+CH₂X₂) of 90% and 83% in CH₄ oxychlorination and oxybromination, respectively (Fig. 8e) [49]. This was ascribed to the promotional effect on HX adsorption on the catalyst due to the presence of solid solutions, thereby enhancing surface reduction. Still, formation of CO_x remains important especially in oxybromination. Further tuning of the catalyst's redox properties could be achieved by supporting nanocrystals of CeO₂ over suitable carriers with low oxide loading (0.5–2 wt.%), as demonstrated by Paunović *et al.* [50]. In particular, CeO₂ supported on magnesium oxide (MgO) could achieve a combined selectivity to bromomethanes of 93% in CH₄ oxybromination (Fig. 8e). This was rationalized based on the ability of the carrier to favor HBr adsorption, which resulted into a decreased oxidizing potential of the CeO₂/MgO system, ultimately reducing activity in side combustion reactions [50]. However, when assessed in CH₄ oxychlorination, CeO₂/MgO resulted into a significant CO_x formation (selectivity ≈ 52%) (Fig. 8e). The reason for the enhanced CO_x generation is found in the over-weakened redox properties of the catalyst, which shifts the operating window of oxychlorination to > 100 K higher temperatures compared to oxybromination, where side chloromethanes combustion reactions take place. Alternatively, the use of trivalent promoters, and especially of rare earth elements, has been shown to reduce the redox properties of CeO₂ in HCl and CO oxidation [16]. This has also been demonstrated in congeneric C₂H₄ oxychlorination, in which mixed oxides of CeO₂ and Eu₂O₃ led to reduced CO_x formation in this reaction [26]. Consequently, promotion and synthesis of mixed oxides of CeO₂ with rare earth elements are possible future directions to be explored in alkane oxyhalogenation.

These results indicate that different catalyst design criteria have to be applied in order to achieve a high selectivity to halomethanes depending on the halogen of choice. To this end, research has been recently focused on alternative strategies, such as embedding redox active metal centers within a matrix featuring mild oxidizing properties. Valid examples are represented by lanthanum vanadates (LaV_yO_z) for CH₄ oxybromina-

tion and lanthanum oxychloride (LaOCl) for CH₄ oxychlorination, as well as europium oxyhalide (EuOX) for CH₄ oxyhalogenation (Fig. 8e) [28,40,44,47,51]. In particular, LaOCl and LaV_yO_z with a specific stoichiometry (LaV_{0.5}O_{2.75}) enable to reach a combined halomethanes selectivity of ca. 90% in oxychlorination and oxybromination, respectively [44,51]. This was elucidated based on the pronounced halogen coverage on the surface of the oxyhalide phase, which in the case of LaV_{0.5}O_{2.75} is due to the excess of lanthanum compared to stoichiometric LaVO₄, thus generating patches of segregated LaOBr phase within a LaVO₄ matrix, which suppresses side combustion reactions [51]. These observations are in line with the results gathered in CH₄ oxybromination over EuOBr (Fig. 8e), whose balanced redox properties enabled to achieve up to 98% selectivity to bromomethanes at relevant CH₄ conversion levels (≤ 30%), thus surpassing any reported system to date [40]. Still, when its oxychloride counterpart (EuOCl) was assessed in CH₄ oxychlorination, a much stronger propensity to CO_x formation (selectivity ≈ 22%) was observed, again related to the shifted operating window to high temperatures where chloromethanes combustion is more prominent as observed for CeO₂/MgO [47].

Recently, research has also been focused on the oxyhalogenation of ethane and propane, the second and third most abundant alkanes in natural gas. In particular, CeO₂ was shown to produce in a single step ethylene (C₂H₄) and propylene (C₃H₆) in the oxychlorination of ethane and propane, respectively, as a result of the dehydrochlorination of intermediate alkyl chlorides [47,48,53,54]. Still, the olefin selectivity was found limited in the oxychlorination of ethane (52%) and propane (31%) at moderate alkane conversion levels (20%), mainly due to the formation of chlorocarbons and CO_x, respectively (Fig. 8f,g) [48]. In order to increase the dehydrochlorination properties and reduce the over-oxidizing propensity in C₂ and C₃ chemistries, respectively, solid solutions of transition metal oxides with CeO₂ were investigated (Fig. 8f and 8g). In particular, MnO_x-CeO₂ was shown effective for the generation of ethylene in ethane oxychlorination, reaching 67% C₂H₄ selectivity, while NiO-CeO₂ was demonstrated as a highly efficient catalyst for C₃H₆ production *via* propane oxychlorination, obtaining ≤ 82% olefin selectivity and up to 55% C₃H₆ yield, rivaling the best performing systems among any propylene generation technology [53–55]. Similarly to the strategies to alter the oxidizing potential, the acidic properties of CeO₂, which have been shown critical in improving the dehydrohalogenation performance in congeneric C₂H₄ oxychlorination, could also be tuned by promotion or synthesis of mixed oxides with rare earth elements [26].

Alternatively, LaOCl has been mainly disclosed in patents for the selective production of vinyl and allyl chloride by ethane and propane oxychlorination, respectively [56,57], while EuOCl has been demonstrated as a highly efficient catalyst, reaching ≤ 97% olefin selectivity in alkane oxychlorination and ≤ 90% C₂H₄ yield in ethane oxychlorination, surpassing any existing C₂H₄ generation route [47]. On the other hand, the use of HBr as halogen source mainly resulted in the formation of alkyl bromides, or formation of cracking and combustion products in

the oxybromination of ethane and propane over CeO₂ and EuOBr (Fig. 8f and 8g) [52]. This was attributed to the alkane activation pathway, which occurs in the gas-phase with evolved Br₂ and Br• radicals, leaving a halogen-free surface that is prone towards cracking and combustion. On the contrary, alkane oxychlorination was shown to occur on a chlorine-rich surface, which results in the observed superior olefin selectivity [58].

4. Conclusions

Sustainable halogen recovery within polymer production and natural gas valorization represents an emerging field for application of ceria-based catalysts. In particular, ceria offers a broad range of possibilities to tune the redox and acid properties that are required to attain the desired activity and selectivity patterns in different types of hydrogen halide oxidation, or alkane and alkene oxyhalogenation, which is unparalleled by any other active phase. Furthermore, ceria offers significant opportunities for bifunctional catalysis and process intensification due to combination of oxychlorination and dehydrochlorination functions in one surface. Nonetheless, strong redox properties of ceria can lead to over-oxidation in these processes, which can be moderated by the degree of halogenation. In combination with the limited stability of the ceria phase at low temperatures or at low-to-moderate oxygen excess in the feed, which is particularly pronounced in catalytic process that involve HBr recycling, this constitutes an inherent challenge for its application. Alternative lanthanide-based catalysts, such as europium oxyhalides could overcome these issues, yet show lower activity than ceria. Overall, we exemplify that the versatility of ceria in halogen chemistry is key for rational catalyst design to meet the requirements for potential wide-spread application.

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Graphical Abstract

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Ceria in halogen chemistry

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Ceria is a prominent catalyst for a great variety of processes in halogen chemistry, such as hydrogen halide recycling, manufacture of halogenated chemical building blocks, and halogen mediated natural gas upgrading.

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卤素化学中的铈

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摘要: 卤素化学是聚合物工业生产中的重要组成部分, 作为一种有吸引力的策略, 它在活化天然气中轻链烷烃方面越来越受到重视. CeO_2 基催化剂在卤化氢回收方面有着令人兴奋的潜力, 这使得基于卤素的小分子活化过程具有高效率. 本文综述了近年来在高分子工业(聚氯乙烯、聚氨酯和聚碳酸酯)和天然气改质中轻烃活化方面应用的铈基催化剂的研究进展, 讨论了铈催化剂的作用机理和面临的挑战, 以期未来催化材料的设计和和应用提供帮助.

关键词: CeO_2 ; 卤化氢; 乙烯; 烷烃; 选择性天然气改质; 氧化; 氧氯化; 氯乙烯

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