

Development of Industrial Catalysts for Sustainable Chlorine Production

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Abstract: The heterogeneously catalyzed gas-phase oxidation of HCl to Cl₂ offers an energy-efficient and eco-friendly route to recover chlorine from HCl-containing byproduct streams in the chemical industry. This process has attracted renewed interest in the last decade due to an increased chlorine demand and the growing excess of byproduct HCl from chlorination processes. Since its introduction (by Deacon in 1868) and till recent times, the industrialization of this reaction has been hindered by the lack of sufficiently active and durable materials. Recently, RuO₂-based catalysts with outstanding activity and stability have been designed and they are being implemented for large-scale Cl₂ recycling. Herein, we review the main limiting features of traditional Cu-based catalysts and survey the key steps in the development of the new generation of industrial RuO₂-based materials. As the expansion of this technology would benefit from cheaper, but comparably robust, alternatives to RuO₂-based catalysts, a novel CeO₂-based catalyst which offers promising perspectives for application in this field has been introduced.

Keywords: Catalytic HCl oxidation · CeO₂ · Chlorine recycling · Cu-based catalysts · Supported RuO₂

Introduction

Chlorine is a highly reactive element, which is principally produced by electrolysis of one of nature's most plentiful and inexhaustible minerals, common salt. For more than 100 years, industry has exploited this compound in a vast range of processes to create thousands of often indispensable industrial chemicals and consumer products.^[1] Even if chlorine represents a major building block of today's chemistry, about one third of all end products do not actually contain it. This implies that about 50% of the Cl₂ employed is reduced to HCl or chloride salts upon use. Two of today's most versatile plastics, polyurethanes (PU) and polycarbonates (PC), exemplify chlorine-free materials produced using chlorine.^[2] The two most relevant polyurethanes are made from toluene or methylene isocyanates, which are prepared according to the reaction sequence depicted in Fig. 1a. Remarkably, 4 mol HCl are generated

per mol of desired product in the phosgenation step. The HCl by-product can be marketed as raw material for the production of 1,2-dichloroethane (EDC), which is the starting compound for the manufacture of PVC. Current market data reveals that the demand for PVC grows at a slower pace than that for PU and PC.^[3] Thus, the excess HCl can no longer be absorbed by the PVC industry. In this scenario, three options are possible, namely, neutralization, selling of dry HCl and/or hydrochloric acid, and recycling. The first obviously is environmentally unattractive. If the second is not feasible, recycling constitutes a smart way to valorize HCl. Electrolytic and catalytic technologies can be applied for this purpose.^[2,4] HCl electrolysis operates in multiple plants worldwide since its commercialization in the 1960s. This methodology is based on the conversion of a 22 wt.% HCl solution over graphite electrodes separated by a diaphragm to Cl₂ and H₂, respectively at the anode and the cathode.^[5] Due to the modular design, the specific capital investments for electrolysis units is little scale driven, but the high energy input needed leads to unfavorable operating costs. The development of oxygen-depolarized cathodes (ODC technology) constitutes a major improvement, enabling power consumption to be reduced by ca. 30%.^[6] The catalytic option is based on the gas-phase oxidation of HCl to Cl₂ by O₂ over a solid material (Fig. 1a). The equilibrium conversion of HCl is favored at low temperature (<700 K), high feed O₂/HCl ratio, and high total pressure. This reaction requires an unbeatably lower energy demand with respect to any kind of elec-

trolysis,^[2] but its realization is characterized by high investment costs, which can be alleviated by maximizing the single line capacity of the whole process.^[3] It is clear that the performance of the HCl oxidation catalyst is crucial in rendering a viable technology. Starting with the original HCl oxidation process by Deacon^[7] till recent times, the industrialization of this reaction has been hampered by the difficulty to obtain sufficiently active and durable catalysts. The original Deacon catalyst, CuCl₂/pumice, suffered from fast deactivation due to volatilization of copper in form of chlorides, operational problems such as particle coagulation, and severe corrosion of plant components.^[7] A later process based on CuCl₂-KCl/SiO₂ (Shell-Chlor process)^[8] was also abandoned due to the poor catalyst activity and lifetime. The Mitsui-Toatsu catalyst, Cr₂O₃/SiO₂,^[9] exhibited improved stability but installation was limited to a single plant.^[2] In the last decade, a major breakthrough in catalytic HCl oxidation has been achieved with the development of RuO₂-based materials, *i.e.* RuO₂/TiO₂^[2,10] by Sumitomo and RuO₂/SnO₂-Al₂O₃^[11] by Bayer. Their distinctive features are the high activity at low temperature and the remarkable stability against (bulk) chlorination. Sumitomo's catalyst has been installed for large-scale chlorine recycling for several years,^[2] whereas Bayer's catalyst has been successfully piloted. Nevertheless, as the expansion of this technology would benefit from the availability of alternative catalysts based on less expensive metals than ruthenium, catalytic HCl oxidation remains an active field of research nowadays. Furthermore,

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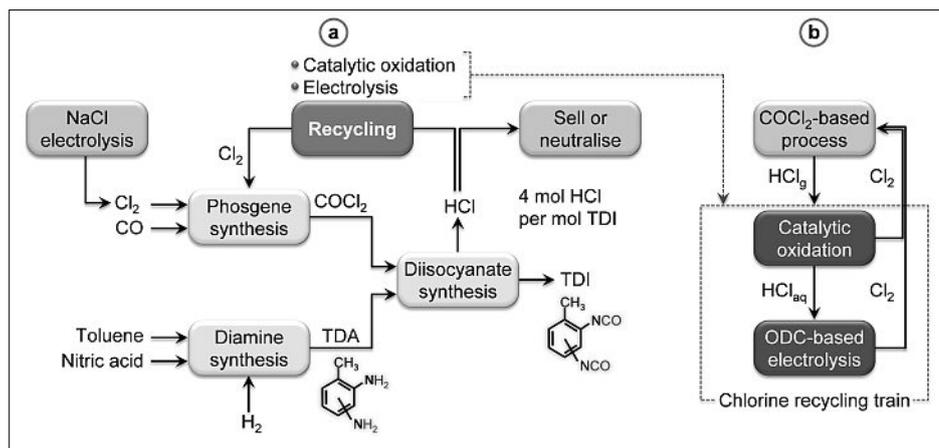


Fig. 1. (a) Simplified flow sheet of the toluene diisocyanate (TDI) production, exemplifying the concept of chlorine recycling. The phosgenation of toluene diamine (TDA) produces 4 mol HCl per mol TDI. Catalytic oxidation and/or ODC-based electrolysis of HCl by-product are attractive options for Cl₂ recovery. (b) Integration of catalytic and electrolytic technologies for high-purity Cl₂ production from HCl. This configuration is attractive for large capacity expansions of phosgene-based processes.

the combination of catalytic and electrolytic technologies for chlorine recycling is an attractive option. In fact, as processing of the HCl byproduct by the equilibrium-limited Deacon reaction cannot lead to full HCl conversion, the optimized ODC-based electrolysis can complement the catalytic route by fully converting the unreacted HCl to Cl₂ (Fig. 1b).

Herein, we provide a concise overview of the catalyst design aspects learnt from the analysis of historical copper-based catalysts and revisit the key milestones of the attainment of RuO₂-catalyzed processes for HCl oxidation. The latter comprised i) a primary screening of materials of different formulations, ii) a more detailed performance assessment of selected systems, including lifetime testing, coupled with characterization of their structural properties and reaction mechanism, and iii) scale up of the most promising catalysts. This last step involves the preparation of catalyst bodies and testing at the pilot scale. Finally, a promising material based on a

cheaper metal than ruthenium, cerium, is introduced which offers exciting perspectives for implementation in industrial chlorine recycling.

Traditional Cu-based Catalysts

As mentioned in the Introduction, historically relevant Cu-based catalysts were reported to undergo deactivation due to chlorination of copper. CuO, CuCl₂, and CuCl catalysts in bulk and supported forms have been investigated in detail to better describe and rationalize these phenomena at the molecular level.

Reaction over CuO/Al₂O₃ was accompanied by discoloration of the catalyst bed and formation of a condensate downstream the reactor, clearly indicating that deactivation was due to the loss of active phase (inset of Fig. 2a). X-ray diffraction (XRD) analysis of used CuO confirmed the almost complete transformation of the original oxide into a mixture of chlorinated phases,

which are known to be volatile at the reaction temperature (Fig. 2b). Even operation at high O₂/HCl ratios could not prevent this, pointing to difficult catalyst reoxidation. Mechanistic investigations in the Temporal Analysis of Products (TAP) reactor indeed indicated that lattice oxygen of CuO actively participates in the oxidation of HCl and that chlorine evolution is highly impeded, thus suggesting that a more active and particularly stable (copper) catalyst could be achieved by controlling the degree of chlorination.^[12b] Furthermore, combination of TAP and XRD data enabled the identification of copper (hydr) oxychloride as the main active phase. An additional stability issue was represented by the coagulation of the catalyst particles. When this occurs, even catalysts exhibiting high activity levels cannot be considered for technical scale, as the excessive pressure drop and channeling determined by this phenomenon would eventually result in plant shut-down.

With the aim to stabilize the copper, there was a recent attempt to trap it in a more complex structure. Thus, various copper spinel and delafossite catalysts were prepared and tested. While spinels still displayed deactivation and/or coagulation (Fig. 2a), the well-crystallized cuprous delafossite (inset of Fig. 2c) showed remarkable long-term stable performance for 1000 h in a single fixed-bed reactor without operational incidents (Fig. 2c).^[13] Still, the original delafossite phase suffered from profound bulk changes under Deacon conditions (Fig. 2b) and the copper content was considerably depleted with time-on-stream (inset of Fig. 2c). In particular, CuAl₂O₄ and CuO were formed by action of O₂ and the oxide was further transformed into the volatile copper chlorides in contact with HCl/Cl₂. In spite of the outstandingly high and stable Cl₂ production exhibited in the long-term testing, the consistent metal loss represents a critical issue for industrial consideration.

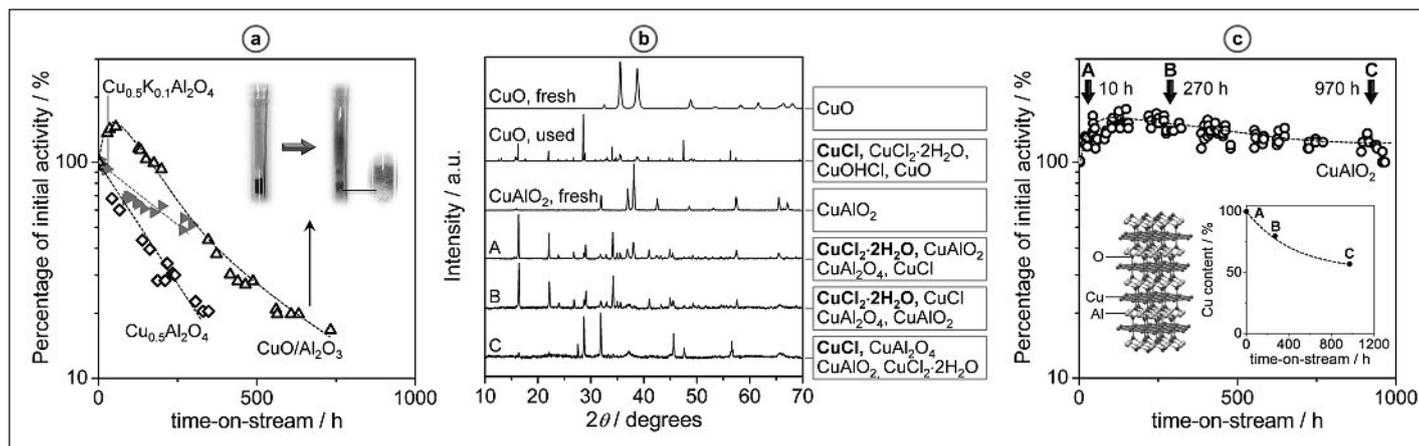


Fig. 2. (a,c) Catalytic performance and (b) XRD patterns of Cu-based catalysts.^[13] The inset in (a) shows the catalyst bed decoloration due to volatilization of active phase, typical for Cu-based materials. The insets in (c) depict the structure and the Cu loss versus time-on-stream for CuAlO₂.

New Generation RuO₂-based Catalysts

Ruthenium's activity for HCl oxidation was claimed as early as 1964,^[14] but only in the last two decades intense research efforts culminated with the industrial implementation of RuO₂-based materials.

RuO₂/TiO₂-rutile was reported by Sumitomo to be 50 times more active than Cu, Cr, Fe, Mn, and Ni catalysts.^[2] Qualitative profiles obtained by temperature-programmed reaction experiments, which highlight the temperature at which Cl₂ production begins,^[12b] evidenced the low-temperature activity of RuO₂. Further measurements showing the dependence of the chlorine production on the temperature, based on the quantitative assessment of the catalyst activity during isothermal tests, confirmed this result and underlined its remarkable activity. Ruthenium-based materials reached even higher Cl₂ production levels with respect to copper- and chromium-based catalysts already at about 100 K lower temperature. Interestingly, the structural properties of the carrier strongly influenced the catalyst's activity. In fact, RuO₂/TiO₂-rutile was ten times more active than RuO₂ supported on other conventional carriers such as titania-anatase, silica, and alumina.^[2] SnO₂-cassiterite, Bayer's support, produced a highly active catalyst as

well.^[11] RuO₂ appeared to be an outstandingly stable phase too. No bulk chemical alterations were detected upon exposure to reaction conditions and even to the sole presence of HCl (Fig. 3a). Nevertheless, ageing of RuO₂/SnO₂ at rather high temperatures determined a loss of 75% of the original activity, which could be largely prevented by addition of alumina to the catalyst formulation.^[11a]

In view of the high potential demonstrated by Ru-based systems and to prepare the basis to undertake optimization, a solid knowledge of bulk and supported RuO₂ was gathered by means of extensive characterization. Mechanistic and kinetic investigations were also carried out following both experimental and theoretical approaches. With regards to bulk RuO₂, XRD analysis indicated that the fresh sample has a rutile structure and that the integrity of the oxide phase is preserved upon use, as mentioned above.^[14] Still, X-ray photoelectron spectroscopy (XPS) evidenced that chlorine is present at the surface of the catalyst after reaction.^[15] Ultra-high vacuum (UHV) surface studies and Density Functional Theory (DFT) calculations on RuO₂(110), the most extended and stable rutile facet, indicated that surface chlorination generates a ruthenium oxychloride (RuO_{2-x}Cl_x) and that this process has a self-limiting nature.^[15,16] Experiments in

the TAP reactor on a polycrystalline RuO₂ sample quantified the chlorine uptake, thus concluding that only *ca.* 75% of the surface Ru sites are chlorinated (Fig. 3b).^[12b] This outcome allowed the outstanding stability of RuO₂ in HCl oxidation to be rationalized. According to spectroscopic studies on RuO_{2-x}Cl_x(110), ruthenium oxychloride was identified as the actual active phase.^[16] A reaction cycle based on a Langmuir-Hinshelwood scheme was proposed on the basis of UHV investigations.^[17] The elementary steps of the reaction, as described by DFT analysis, are: i) hydrogen abstraction from HCl by adsorbed atomic oxygen and adsorption of the Cl atom, ii) recombination of surface Cl atoms and Cl₂ desorption, iii) recombination of surface hydroxyl groups and water desorption, iv) surface regeneration by dissociative oxygen adsorption.^[15] Both experimental and theoretical studies pointed to chlorine evolution as the most hampered step and, therefore, under practical conditions, catalyst reoxidation is rate limiting. TAP experiments, separating chlorination and oxidation, evidenced a tight dependence of the net Cl₂ production on both Cl and O coverages, thus extending the validity of a Langmuir-Hinshelwood mechanism for HCl oxidation from model surfaces to realistic polycrystalline samples.^[12a] Recently, structure-mechanism relation-

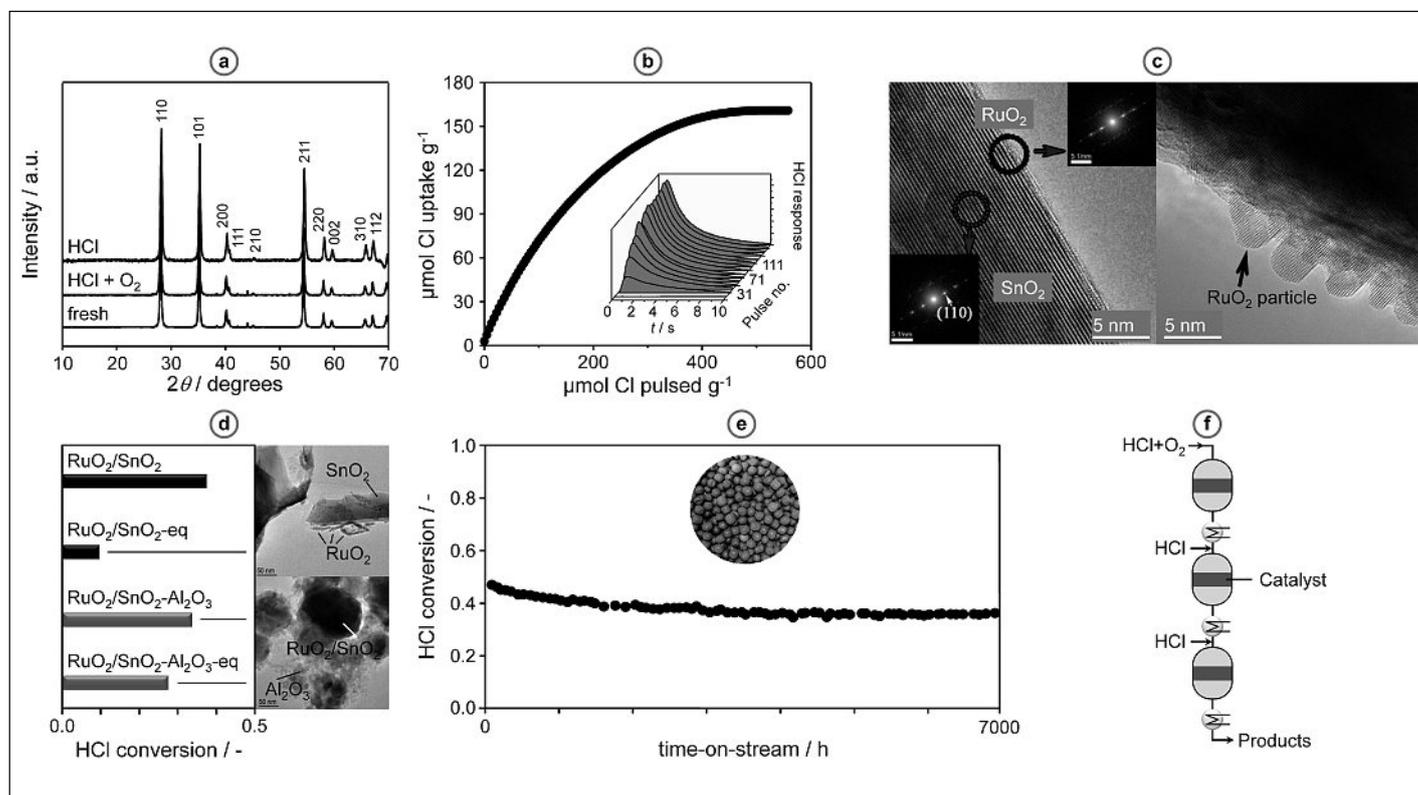


Fig. 3. Catalytic and characterization studies of RuO₂-based catalysts. (a) XRD patterns of fresh and used RuO₂.^[15] (b) Chlorination profile of polycrystalline RuO₂ determined by controlled doses of HCl at 573 K in the TAP reactor.^[12a] (c) Morphology of RuO₂/SnO₂ visualized by TEM.^[11a,21] (d) Studies of the deactivation mechanism of RuO₂/SnO₂ and of the stabilizing effect of the Al₂O₃ binder.^[11a] (e) Long-term stability of RuO₂/SnO₂-Al₂O₃ upon pilot testing with 2-mm granules (inset).^[11a] (f) Bayer's adiabatic reactor cascade with intermediate heat exchangers.

ships have been established on the basis of catalytic and TAP data, which explain the superior performance of RuO₂ with respect to other metal oxides based on three crucial catalyst features: limited surface chlorination favoring stability, fast Cl₂ evolution, and rather easy re-oxidation, allowing low-temperature operation.^[12c] The latter characteristic has also been highlighted by DFT.^[18] Microkinetic analysis indicated that HCl oxidation is structure sensitive. In particular, the activity of the three main rutile surfaces follows the order (110) > (101) > (100).^[19] With respect to supported RuO₂-based catalysts, the effect of the carrier nature on activity could be understood by means of Transmission Electron Microscopy (TEM) imaging. Sumitomo showed that RuO₂ on TiO₂-anatase assumes the form of well-distributed nanoparticles, while it fully covers TiO₂-rutile as a thin film.^[2] The latter outcome was explained on the basis of the lattice matching of RuO₂ and TiO₂, which makes it possible for RuO₂ to epitaxially grow over TiO₂-rutile. High-temperature treatments of rutile-type carriers have been often applied to ensure the formation of the rutile structure at the surface level and thus favor this type of deposition. Analysis of RuO₂/SnO₂-cassiterite produced similar results to the RuO₂/TiO₂-rutile case.^[11a] The carrier's grain appeared uniformly

covered by RuO₂ nanostructures, which assume the form of a thin layer as well as more defined protruding nanoparticles (Fig. 3c). Other supports would favor RuO₂ deposition as particles. The epitaxial growth of the active phase on the carrier, maximizing the metal dispersion and the contact with the support, explains the superior performance of RuO₂/TiO₂-rutile and RuO₂/SnO₂ both in terms of activity and stability. Nevertheless, both materials deactivate in the long term. This phenomenon has been related to RuO₂ sintering. In the case of the Bayer catalyst, large aggregates of RuO₂ are indeed visible in the TEM images of the aged catalyst sample (Fig. 3d). Nanosized silica added to RuO₂/TiO₂-rutile proved to prevent deactivation by avoiding intra-particle RuO₂ crystallites migration,^[2] while the presence of alumina in RuO₂/SnO₂ could stabilize the active phase majorly addressing the inter-particle interaction and agglomeration (Fig. 3d).^[11a] The mechanistic fingerprints of HCl oxidation appeared substantially preserved when supporting RuO₂ on a carrier.^[12a,19] Microkinetic calculations indicated that the activity depends on the number of layers of RuO₂ coating SnO₂. A single monolayer does not produce a significant amount of Cl₂, while a bilayer attains higher activity than the RuO₂(110) surface.^[18] Steady-state Deacon kinet-

ics on SnO₂-supported RuO₂ indicated a medium-to-strong positive effect of the partial pressures of reactants and deep inhibition by both water and chlorine products.^[19] *In situ* Prompt Gamma Activation Analysis (PGGA) supports that adsorbed Cl poisons the surface.^[19] Recently, the use of this technique and the TAP reactor to determine the surface coverage of Cl and O species on RuO₂ during HCl oxidation, coupled with theory, have been instrumental for studying the fundamental origin of compensation phenomena in heterogeneously catalyzed processes.^[20]

The next step comprised the development of a technical catalyst, which involves the adaptation of laboratory protocols for a large-scale manufacture and shaping of the catalyst powder into mm-sized bodies. Starting with one of the two most successful catalysts, RuO₂/SnO₂, and based on the knowledge derived by its characterization in powder form, i) pretreatment of the cassiterite support at high temperature prior to impregnation of the active phase, to favor epitaxial growth, and ii) application of a low calcination temperature, to minimize sintering of the deposited RuO₂, resulted in key procedural requirements for the synthesis of a successful industrial catalyst.^[11a,21] Another relevant point was the necessity to incorporate the alumina binder, whose role as stabilizer of the RuO₂ phase has been stressed above, before impregnation of the active phase and shaping. In fact, the latter step is completed by hardening of the pelletized catalyst at high temperature and this would cause excessive RuO₂ agglomeration or loss in form of volatile RuO₄.^[3] In order to attain an efficient preparation, the binder had to be accurately chosen to avoid unselective deposition of the active phase, *i.e.* on the binder rather than on the carrier. In this respect, the surface acidity of the carrier is one decisive parameter for optimal RuO₂ incorporation.^[3] Pressed spheres of RuO₂/SnO₂-Al₂O₃ exhibited long-term stability upon pilot testing (Fig. 3e).^[11a] After a slight loss of activity in the first 1000 h of the run, the HCl conversion level remained constant for more than 7000 h on stream. This result confirmed the suitability of this catalyst for application to large-scale chlorine production.

In designing a suitable reactor, the main challenges are temperature control, due to the exothermicity of HCl oxidation, and the sensitivity of RuO₂ to activity loss by sintering. Two reactors have been developed for the RuO₂-based materials. Sumitomo opted for a multi-tubular fixed-bed reactor.^[2] RuO₂/TiO₂/SiO₂ is placed in parallel tubes which are cooled by a circulating heat transfer salt. The tubes are filled with a catalyst of staged activity and the reactor shell is partitioned into several

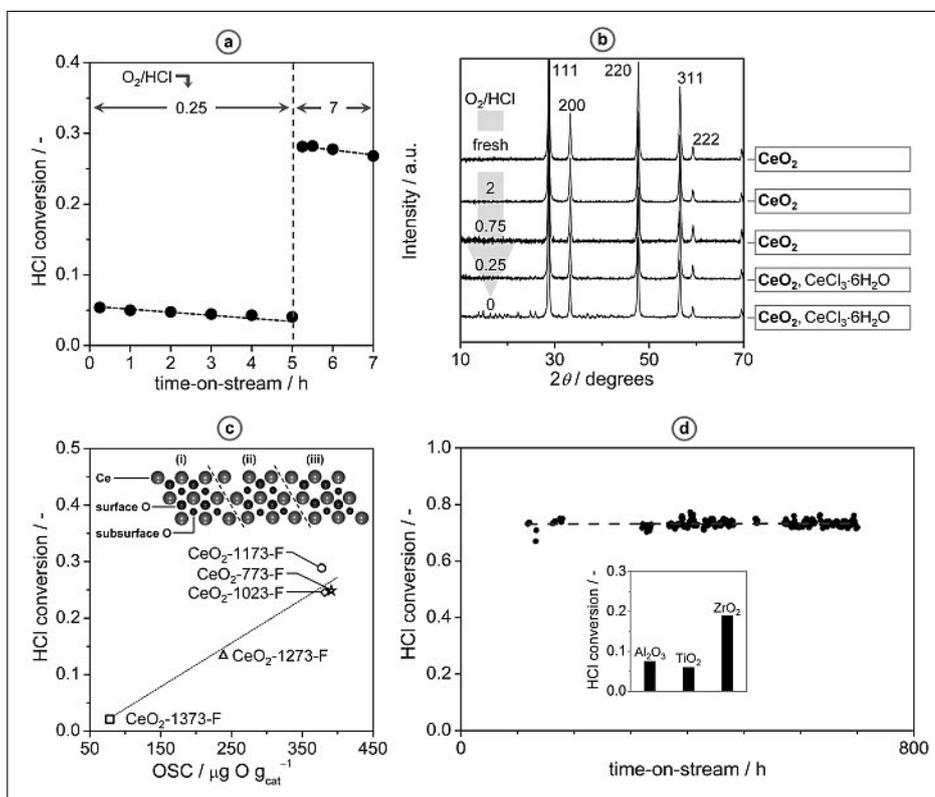


Fig. 4. (a) Catalytic performance of CeO₂ at different feed O₂/HCl ratios.^[25] (b) XRD patterns of fresh and used CeO₂.^[25] (c) Activity dependence on OSC for CeO₂ samples.^[25] The inset shows structural models of a p(2x2) supercell of CeO₂(111): (i) regular surface, (ii) surface vacancy, and (iii) subsurface vacancy. (d) Effect of the carrier nature on the activity of supported CeO₂ (inset) and long-term stability of CeO₂/ZrO₂ upon pilot testing.^[26]

zones in order to ensure a constant temperature profile along the whole reactor.^[22] This reactor design is elegant but implies high technical complexity. Bayer followed the alternative concept of a multi-stage adiabatic fixed-bed cascade (Fig. 3f).^[23] The rise in temperature is in this case controlled by an adequate splitting of the HCl feed to the stages constituting the cascade and by removal of the heat of reaction between each stage with heat exchangers above the dew point of the gas mixture. The complexity of such a reactor cascade is comparably low.

Sumitomo has licensed a plant based on their technology with a capacity of 100 kton per year to a Japanese chemical manufacturer in 2002, followed by three additional plants worldwide.^[2] Bayer's catalyst and reactor cascade successfully concluded the pilot stage and is ready for plant implementation.^[3]

CeO₂-based Catalysts as a Promising Alternative

As mentioned in the Introduction, the main drawback of the use of ruthenium is its high and fluctuating market price. This issue can be approached by two main strategies: maximizing the ruthenium specific activity or finding less expensive but comparably stable alternatives to RuO₂-based catalysts. A promising result in the latter direction has been recently accomplished.

CeO₂, which is widely used in oxidation reactions, has been recently claimed in the patent literature to be active for HCl oxidation.^[24] This encouraging premise has triggered an in-depth study of bulk CeO₂.^[25] Ceria can be categorized as a high-temperature catalyst. Limited bulk chlorination was observed under HCl-rich conditions (O₂/HCl ≤ 0.25), inducing activity loss, but the bulk chloride phase rapidly and completely disappeared when the catalyst was exposed to O₂-rich conditions, which restored the initial activity (Fig. 4a,b). XPS and thermogravimetric studies indicated that at O₂/HCl ≥ 0.75 only the outermost surface layers of CeO₂ contain chlorine. The activity of CeO₂ appeared linearly related to the presence of oxygen vacancies in the material (Fig. 4c). Cl activation from vacancy positions to surface Ce atoms was computed as the most energy-demanding step, although chlorine-oxygen competition for the available active sites renders reoxidation as the rate-limiting step. In view of its remarkable performance, further steps towards the practical implementation of this catalyst are being undertaken.^[26] Herein, we briefly introduce still unpublished data regarding these developments. Differently supported CeO₂ catalysts have been syn-

thesized by dry impregnation. Zirconia was demonstrated to be a better carrier than alumina or titania. CeO₂/ZrO₂ in fact attained 2–3 times higher HCl conversion than CeO₂ on the two other supports (inset of Fig. 4d). Characterization data indicates that, while CeO₂ appears in form of large nanoparticles over TiO₂ and Al₂O₃, thin films of CeO₂ as well as solid solutions of Ce and Zr are present in CeO₂/ZrO₂. In the latter case, the structural features identified would be responsible for both a high dispersion and an increased amount of oxygen vacancies,^[27] thus explaining the superior activity of CeO₂/ZrO₂. This catalyst has been pilot-tested in technical shape to evaluate its lifetime in the same adiabatic cascade used for RuO₂/SnO₂-Al₂O₃ (Fig. 3f). The flat profile of the HCl conversion over 700 h on streams (Fig. 4d) confirms its robustness and provides excellent perspectives for its concrete use as alternative to RuO₂-based systems.

Conclusions

The catalyzed oxidation of HCl is a sustainable route for Cl₂ recycling. After many decades of limited success, RuO₂-based catalysts have been developed which appear to satisfy the long-term industrial need for sufficiently performing materials. In view of the highly corrosive nature of the reaction mixture and the exothermicity of the reaction, the core challenge to be addressed at different scales was catalyst lifetime. We have shown that a fundamental understanding of the catalytic systems was vital to succeed. Recent studies have identified a ceria-based catalyst exhibiting adequate activity and long-term stability to promote its further application at industrial scale. The use of this more cost-effective material may favor the expansion of the catalytic chlorine recycling technology.

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