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Catalytic selective oxidation: The forefront in the challenge for a more sustainable chemical industry

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ABSTRACT

This short review documents some examples of recent innovations in the field of catalytic selective oxidation. The processes that are currently being developed for propene oxide are described, highlighting innovative aspects that contribute to a better sustainability of the chemical industry. The target of closing the chlorine cycle, one of the main problems in the modern chemical industry, is also discussed, with the aim of highlighting the important role of catalytic oxidation.

1. Introduction: how catalytic oxidation contributes to the common effort for a more sustainable chemical industry

Oxidation catalysis has been and will be playing a leading role in the ambitious project of a more sustainable industrial chemistry [1–30]. In fact, oxidation is one of the reactions with the greatest potential for improvement, and in recent years this has led to the development of a series of better processes, as has been widely documented in various books and papers.

However, despite the remarkable scientific achievements and successful industrial implementation of several technologies, some processes still co-produce large amounts of waste, or operate under conditions leading to non-optimal selectivity of the desired compound. Some targets evidencing the possible role of catalytic selective oxidation in the years to come for the development of a more sustainable chemical industry are: (a) new approaches for the generation of the oxidant and use of alternative oxidants; (b) activation of light alkanes at mild conditions, and oxidation at terminal C atoms; (c) direct synthesis of hydrogen peroxide by oxidation of hydrogen and its *in situ* use as a viable route for more economical electrophilic oxidations; (d) alternative reactor configurations and alternative modes for contacting reactants; (e) valorisation of bioplatform molecules by means of catalytic oxidation; (f) new catalysts made of supported nanoparticles for efficient oxidations at mild conditions, and (g) make the chlorine cycle in the chemical industry more efficient, by means of direct use of HCl as co-reactant in oxychlorination reactions.

More specifically, some important guidelines for research and development in the area of catalytic selective oxidation can be summarised as follows:

1. New processes for the synthesis of intermediates and monomers from alkanes by means of oxidative processes, replacing alkenes and aromatics, the traditional building blocks for the petrochemical industry. Examples are shown in Table 1, compiling the several reactions investigated, and the best results achieved so far for each of them, in terms of yield and selectivity [31–53]. Some of them have now become commercial processes, whereas for others the targets of yield or selectivity necessary to make them economically viable alternatives have not yet been achieved.
2. New types of heterogeneous catalytic systems for liquid-phase oxidations, that may allow the use of environmentally friendly oxidants, i.e., hydrogen peroxide and air, in place of oxidants such as nitric acid, permanganate or chromate. Table 2 shows some successful examples that have been recently implemented, or are under investigation [54–76].
3. The use of reaction conditions that make possible decreasing the amount of waste in vent or purge streams, thus considerably lowering the environmental impact of the process. In this context, one relevant example is the shift from air-based, once-through processes to oxygen-based recycling processes, and the corresponding change from reactant-lean to oxidant-lean processes. This not only considerably reduces the emissions and makes purge streams more concentrated and therefore more easily combusted, but may also lead to improved selectivity and productivity. Worthy of note is that in many cases the passage from the conventional reactant-lean to the innovative recy-

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Table 1

Catalytic selective oxidation of alkanes to (petro)chemicals: status and hurdles.

Reaction	Best available catalyst	Best results (from the open literature)	Ref.	Status of the technology	Hurdles to industrial implementation or margins for improvement
Methane to methanol with SO_3	Pd complexes Pt complexes	Conversion 90%, selectivity to methylbisulfate 81%	[35]	Research	Corrosive reaction medium, separation
Methane to formaldehyde with O_2	V_2O_5–SiO_2 MoO_3–SiO_2 Fe_2O_3–SiO_2 SiO_2 No catalyst	Conversion 89%, selectivity 56%, in a recycle reactor (catalyst V_2O_5–SiO_2); Conversion 50%, selectivity 49% in a recycle reactor (catalyst SiO_2)	[36,37]	Research	Low per pass yield (maximum 4%). Higher yields were reported but were not confirmed
Methane to syngas with O_2	Supported noble metal (e.g.: Rh,Pt-support)	Conversion 93%, selectivity 97% (CO), 95% (H_2) (catalyst Rh/Ni-Mg/Al/O); Conversion 80%, selectivity 92% (CO), 96% (H_2) (catalyst Rh/MgO)	[38,39]	Demonstration unit (Snamprogetti)	Technology to be optimised
Methane to ethane and ethene with O_2	Rare earth oxides. Alkaline earth metal oxides: SrO/La_2O_3 Mn/Na_2WO_4–SiO_2	Conversion 20%, selectivity to ethane + ethene 80%	[40,41]	Research	Low yield, catalyst deactivation at high *T*, bad economics
Ethane to acetic acid with O_2	$Mo_1V_{0.25}Nb_{0.12}Pd_{0.0005}O_x$	Conversion 10%, selectivity 78%	[42]	Demonstration unit (34,000 tpy, SABIC, since 2005)	Economics still uncertain
Ethane to ethene with O_2	Ni/Nb/O $MoV_{0.3}Te_{0.23}Nb_{0\cdot 12}O_x$	Conversion 66%, selectivity 88%; Conversion 87%, selectivity 84%	[43,44]	Research	Still economically unfavourable compared to steam-cracking
Ethane to acetonitrile with NH_3/O_2	Co-ZSM-5	Yield 25%	[45]	Research	Low yield
Ethane to vinylchloride with HCl/O_2	$CuCl_2/KCl/CeCl_4$-support	Conversion 95%, yield to VCM 30%	[46]	Pilot plant (INEOS, 1000 tpy)	Many chlorinated by-products, complex separation, corrosive reaction conditions
Propane to propene with O_2	VO_x-MCF	Conversion 41%, selectivity 68%	[47]	Research	Low yield
Propane to acrylic acid with O_2	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$	Conversion 80%, selectivity 61%	[48]	Research	Still economically unfavourable compared to the two-step process from propene
Propane to acrylonitrile with NH_3/O_2	$Mo_{0.6}V_{0.187}Te_{0.14}Nb_{0.085}O_x$	Conversion 86%, selectivity 72%	[49]	Commercial (Asahi Kasei, 70,000 tpy; catalyst Mo/V/Nb/Sb/O)	Economics related to the value gap between propane and propene
Propane to propene oxide with H_2/O_2	Dual-bed catalyst: Au–TiO_2 + Au/TS-1	Conversion 2%, selectivity 8%	[50]	Research	Low yield and selectivity
n-Butane to maleic anhydride with O_2	$(VO)_2P_2O_7$	Conversion 75–85%, selectivity 65–73% (in function of the technology adopted)	[51]	Commercial (several plants)	Margins exists for selectivity improvement
Isobutane to methacrylic acid with O_2	Keggin polyoxometalates	Conversion 10–13%, selectivity to methacrolein + methacrylic acid 70–73%	[10]	Under investigation	Low yield and low catalyst stability
n-Pentane to maleic and phthalic anhydrides with O_2	$(VO)_2P_2O_7$	Conversion 70%, selectivity to phthalic + maleic anhydrides 75%	[52]	Under investigation	Worse economics compared to *n*-butane and *o*-xylene oxidation
n-Hexane to adipic acid with O_2	CoAlPO-18	Conversion 9.5%, selectivity 34%	[53]	Under investigation	Low yield; results not confirmed by other authors

Table 2
Some recent achievements in liquid-phase oxidations with clean oxidants: catalysts and processes.

Reaction	Catalyst	Status	Catalytic performance	Ref
Propene epoxidation with H_2O_2 (HP)	TS-1	Commercial (BASF/Dow 300,000 tpy; Evonik/Uhde 100,000 tpy)	HP conversion > 99%, selectivity (on HP basis) > 95%	[5,54–57]
Propene epoxidation with $H_2 + O_2$	Pd/TS-1 (liquid phase) $Au/Ba(NO_3)_2–TiO_2–SiO_2$ (gas phase)	Research	Conversion 1.4%, selectivity 94%; Conversion 8%, selectivity 91%	[54,55]
Propene epoxidation with cumylhydroperoxide (CHP)	Ti-mesoporous silicate	Commercial (Sumitomo, two plants)	CHP conversion > 95%, selectivity (on CHP basis) > 95%	[54,58,59]
n-Hexane to adipic acid with O_2	Co-AlPO-18	Research	Conversion 9.5%, selectivity 34%	[53,60]
Cyclohexane to adipic acid with O_2	Mn^{II} + NHPI	Pilot unit (Daicel)	Conversion 73%, selectivity 73%	[61–63]
Cyclohexane to adipic acid with O_2 (without solvent)	Fe-AlPO-31	Research	Conversion 7%, selectivity 65%	[64]
Cyclohexene to adipic acid with HP	Na_2WO_4 and PTC	Research	Conversion 90%, selectivity > 99%	[65]
Cyclohexanone to cyclohexanoneoxime with HP	TS-1	Commercial, 60,000 tpy caprolactame (Sumitomo)	Conversion 100%, selectivity > 99%	[66,67]
Cyclohexanone to caprolactone with O_2 and benzaldehyde	$Mn_{0.04}Al_{0.96}PO_4$-36	Research	Conversion 78%, selectivity 98%	[22,68]
Ketones to lactones with HP (cyclohexanone to caprolactone)	Sn-β	Research	Conversion 53%, selectivity > 98%	[69]
Benzene to phenol with CO and O_2	P/Mo/V/O (Keggin polyoxometalate)	Research	Conversion 30%, selectivity 90%	[70]
Benzene to phenol with HP (with sulfolane and water solvents)	TS-1	Research	Conversion 15%, selectivity 85%	[7,71,72]
Benzene to phenol with N_2O (integrated with N_2O production in adipic acid plant)	Fe-HZSM-5	Pilot plant (Solutia-BIC)	Conversion > 40%, selectivity > 95%	[73]
p-Xylene to terephthalic acid with O_2	$Co^{II}–Mn^{II}$ + NHPI	Research	Conversion > 99%, selectivity 82%	[61]
p-Xylene to terephthalic acid with O_2 (without bromine and acetic acid)	CoMn–AlPO-36	Research	Conversion 83–85%, selectivity 80–83%	[74]

cling processes has been possible only after a modification of catalyst composition, allowing operation under more demanding conditions while keeping high selectivity of the desired product. Examples of technologies that have moved from air to oxygen feed are: (a) in the gas phase, the oxychlorination of ethane to 1,2-dichlorethane and the epoxidation of ethene; and (b) in the liquid phase, the oxidation of cyclohexane to cyclohexanol/cyclohexanone and the oxidation of *p*-xylene to terephthalic acid.

4. The integration of oxidation technologies either with upstream processes for the synthesis of the oxidant, or with downstream transformations of the oxidized product. Integration may allow considerable savings in operative costs, reducing the number of unit operations that are usually needed for intermediates purification and storage and decreasing operating costs. Examples include: (a) the synthesis of hydrogen peroxide and its use for propene epoxidation, developed by Solvay-BASF/Dow and by Headwaters-Evonik/Uhde; (b) the oxidation of ethane to acetic acid and its use for the synthesis of vinyl acetate, developed by Sabic; (c) the epoxidation of ethene to ethene oxide and its hydrolysis to ethane diol, developed by Shell; (d) the co-generation of N_2O in adipic acid synthesis and its use as an oxidant for the transformation of benzene to phenol, developed by Solutia/Boreskov Institute of Catalysis; (e) the epoxidation of propene and the use of propene oxide for the synthesis of polyether polyols; (f) the oxidation of *n*-butane to maleic anhydride and the hydrogenation of the anhydride to tetrahydrofuran, developed by DuPont; and (g) the oxidation of ethene to acetic acid and the reaction between acetic acid and ethene to yield ethylacetate, developed by Showa Denko.

2. Improved and new oxidation processes recently implemented at an industrial level: the example of light epoxides

There is no doubt that during the last 10 years the production of light epoxides has yielded the most important industrial achievements [54,77–79]. For instance, Shell Global Solutions recently licensed two plants of the OMEGA (Only Mono-Ethylene Glycol Advanced) technology for MEG (ethane diol) synthesis, that were successfully started up in Korea in May 2008 (400,000 tpy, owned by Lotte Daesan) and in Saudi Arabia in April 2009 (600,000 tpy, owned by Petro Rabigh). A third plan is due to come onstream in Shell Eastern Petrochemicals Complex in Singapore in 2010 (750,000 tpy). MEG is an ingredient for polyester fibres and film, polyethylene terephthalate (PET) resins and engine coolants. In the OMEGA process, the selectivity to ethene oxide (EO) in ethene epoxidation is nowadays close to 90%, considerably higher than that obtained during the 1980s [78]. Reduction of investment costs for the EO plant have been reached by combining several technological improvements (e.g., substituting water for kerosene as reactor cooling medium, redesigning the O_2/hydrocarbon mix nozzles, that also allowed an increase of process safety) with an increase

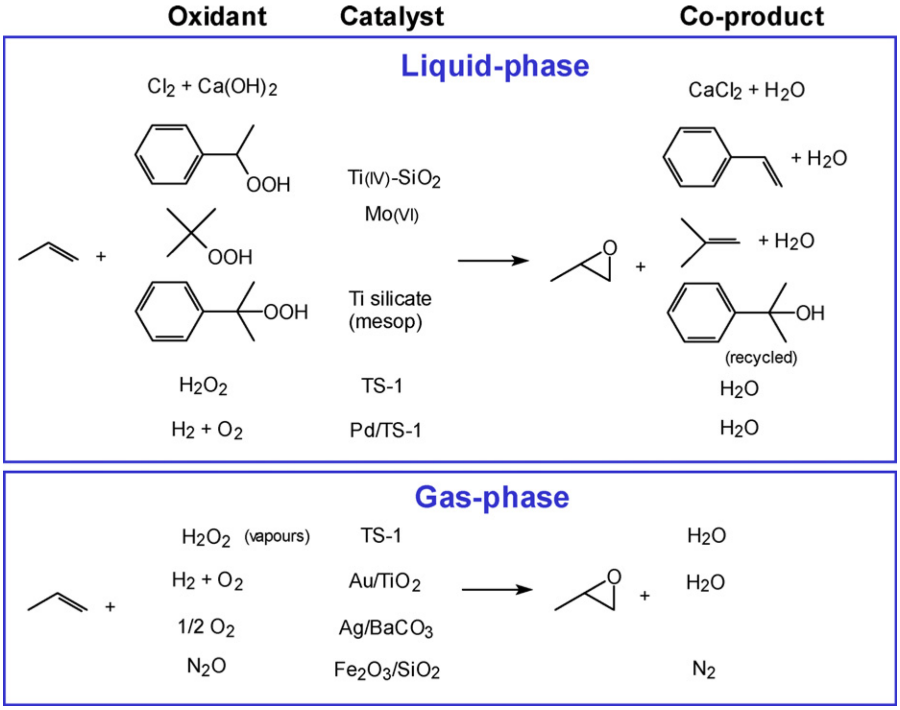

Fig. 1. Several reactions for PO synthesis.

in plant size. The OMEGA process then converts EO to MEG by means of a two-step catalytic route, as opposed to the traditional thermal conversion that converts EO to ethane diol in a single, non-catalytic hydration step. In the thermal process, the ethane diol that is formed also reacts with EO, forming dimeric and trimeric by-products (selectivity around 10 wt%). The OMEGA technology avoids the excess water by performing the hydration in two steps: first converting EO to ethene carbonate by reaction with CO_2, and then hydrolyzing the carbonate to ethane diol and CO_2; using this process, the co-presence of EO and ethane diol is avoided, and the final amount of by-products formed is less than 1%. This technology was originally developed by Mitsubishi, but Shell improved it and integrated it with its own epoxidation process.

Current worldwide propene oxide (PO) production is approximately 6 million tpy. Two technologies dominate the market: hydroperoxidation and the chlorohydrin process (Fig. 1). The styrene–monomer–PO hydroperoxidation process uses a titanium-on-silica epoxidation catalyst; PO is co-produced with styrene. For instance, this process is practiced by Shell in five plants with an overall installed capacity of over 1,100,000 tpy of PO and 2,500,000 tpy of styrene. The process consists of (a) the auto-oxidation of ethylbenzene to EB hydroperoxide, (b) oxygen transfer to propene to produce PO and methylphenylcarbinol, and (3) dehydration of methylphenylcarbinol to styrene. Over the years many improvements have been applied to the SMPO technology to reduce its stress mark in terms of resource utilisation, wastewater production, emission of CO_2, overall variable costs for feedstock and energy and also investment costs by process simplifications [79].

However, even more interesting results have been obtained with the so-called PO-only production processes. In April 2003, Sumitomo Chemical commercialised the first “PO-only” plant in Japan, which produces PO by oxidation of propene with cumyl hydroperoxide, the latter being obtained by hydroperoxidation of cumene [89]. This process is a variant of the SMPO process, which uses cumene instead of ethylbenzene and recycles the co-product cumyl alcohol via dehydration to α-methylstyrene and hydrogenation back to cumene. The characteristic of the process is the large cumene inventory, which serves as the oxygen carrier; due to the high stability of cumyl hydroperoxide, the overall cumene loss is minimal. Moreover, as cumyl hydroperoxide is a stable compound, cumene hydroperoxidation is more selective than ethylbenzene hydroperoxidation. The epoxidation reaction is catalyzed by a proprietary Ti-containing mesoporous silicon oxide catalyst.

Processes recently implemented at the commercial level are the hydroperoxidation processes developed by BASF/Dow and by Degussa-Evonik/Headwaters, both using aqueous solutions of H_2O_2 (HP) as the oxidant for propene (HPPO process) [5,54–57]. The largest plant using this new process with a capacity of 300,000 tpy was built in Antwerp, Belgium, by BASF/Dow, and had been started-up by the end of 2008. The plant is integrated with a 230,000 tpy plant for the synthesis of HP by conventional anthraquinone-based technology. Integration of the two plants allows a significant reduction of transportation costs, and in general offers opportunities for the reduction of HP production costs through economy of scale.

In the BASF/Dow process, the aqueous HP and methanol are introduced into a fixed-bed epoxidation reactor containing a Ti silicalite catalyst (TS-1); PO yield based on propene is estimated to be around 95 mol%. Major by-products are 1,2-propanediol and methoxypropanols formed by the methanolysis of the oxirane ring, which may further react with PO to yield dipropeneglycol monomethylethers. The process is claimed to reduce wastewater by about 75% and energy consumption by about 35%; the building capital cost is about 25% lower than conventional PO plants.

The HPPO plant built by Evonik in Ulsan, South Korea, in cooperation with Uhde and licensed to SKC, has a capacity of 100,000 tpy of PO. In this case, the process also uses a Ti silicalite catalyst, and is supplied with HP from a conventional anthraquinone plant belonging to Degussa/Headwaters, also located in Ulsan. The main technology improvement is due to the use of a shell-and-tube reactor which is an entirely new design; the configuration guarantees a good removal of the reaction heat as well as efficient flow characteristics in each tube, bringing about a high selectivity to PO. A second improvement of this process is the efficient separation of unconverted propene and methanol solvent from PO by the mean of decompression and distillation.

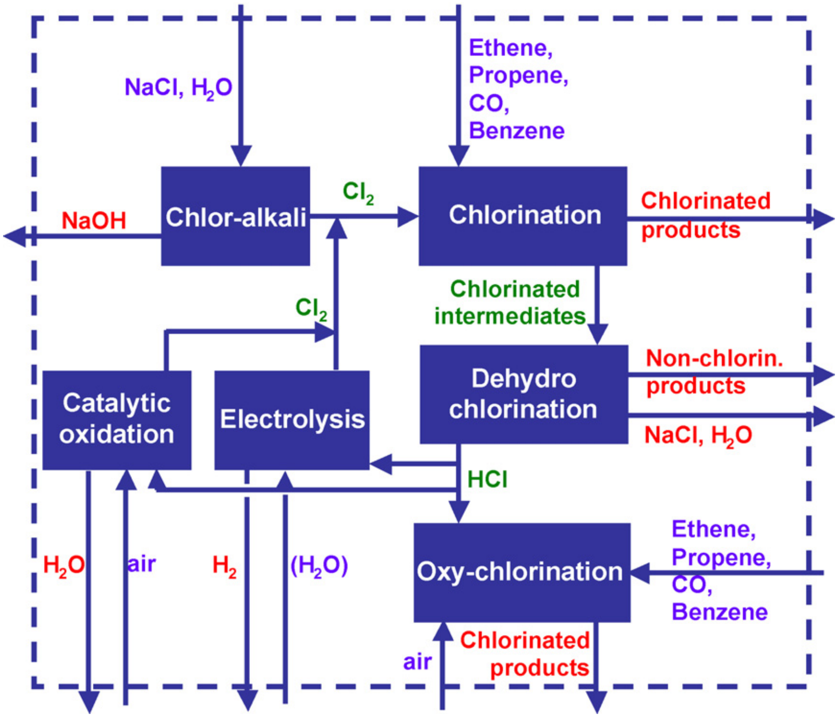

Fig. 2. Scheme illustrating the various possibilities for integration of processes co-producing HCl with processes using HCl.

However, other approaches are currently being studied for PO synthesis (Fig. 1):

1. The *in situ* production of HP from the reaction between hydrogen and oxygen, to be coupled with the epoxidation process, without intermediate concentration or purification of the HP (hydro-oxidation). This might allow a reduction of investment costs, eventually compensating for the higher raw material costs (the selectivity to HP based on hydrogen is lower than that achieved in the conventional anthraquinone-based process).
2. In theory, it should be possible to obtain PO through the direct oxidation of propene with oxygen, similar to the industrial production of ethene oxide. However, the rate of the complete oxidation of propene is very high and this finally leads to a poor selectivity of PO. A vast amount of scientific literature exists on the subject of propene oxidation with O_2; catalysts based on supported Ag have been investigated by ARCO (now Lyondell), and by several academic groups [54]. Other types of catalytic systems investigated include Ti(IV) either supported or incorporated within various crystalline siliceous matrixes. A variant of this process is the use of a co-feed of H_2 and O_2 (hydro-oxidation). The best systems for this reaction are based on Au nanoparticles supported either by TiO_2 (anatase), or by microporous or mesoporous Ti-silicates (TS-1, Ti-MCM41, Ti-β, Ti-SiO_2, Ti-TUD, silylated titanosilicate). The pioneer in this field was the group of Haruta [55,80]. Many studies have been published concerning novel procedures for the preparation of Au-based systems, including various types of support and the use of other metal active components, e.g., Ag, Pd, or Pt. A commercially viable process would require a propene conversion >10%, a PO selectivity >90% based on propene, and >50% based on hydrogen [5,54].

The different approaches used for PO production are an emblematic example of how the discovery of new catalysts and catalytic technologies can lead to the development of innovative processes. Some of the approaches investigated are clearly more sustainable than older technologies, since they adopt concepts like process integration, or avoid the synthesis of co-products. Others still need considerable improvement in order to become economically viable, like the direct oxidation with oxygen or the hydro-oxidation.

3. The role of catalytic oxidation in the aim of closing the chlorine cycle in the chemical industry

An overall chlorine balance for the chemical industry, that considers the flows of chlorine into products and wastes, as well as the recycling of chlorine in the chemical manufacturing sector, indicates that of the 42 million tpy Cl_2 currently produced, approximately half is reduced to HCl or chloride salts, however, roughly one third finally winds up as waste [81,82] (Fig. 2). In fact, various chlorinated intermediates are used for the production of a number of compounds that in the end do not contain Cl: (a) toluene diisocyanate (TDI) and methylene-diphenyl diisocyanate, produced by reacting the corresponding diamines with phosgene; (b) aniline, when obtained by a reaction between chlorobenzene and ammonia; (c) propene oxide, when produced by the dehydrochlorination of chlorohydrin; (d) epoxy resins, synthesized by the reaction of epichlorohydrin with bisphenol A; (e) phenol, when produced by hydrolysis of chlorobenzene by caustic soda; and (f) fluorocarbons and hydrofluorocarbons, produced by stoichiometric or catalytic dechlorination of chlorofluorocarbons. Other important sources of hydrogen chloride are the manufacture of fertiliser materials from potassium chloride and sulfuric acid, and the production of white pigments.

The transformation of the chlorinated intermediates into the final product leads to the release of HCl, which is usually neutralized to get waste chlorinated salts, e.g., $CaCl_2$ or NaCl (Fig. 2). In some cases, however, integration of the above mentioned technologies with processes which finally incorporate chlorine in the product is possible. For example, often the synthesis of diisocyanates (TDI) or epichlorohydrin is integrated with the vinyl chloride synthesis, in which oxychlorination of ethene is carried out using the HCl produced both from 1,2-dichloroethane (DCE) cracking to VCM and from the TDI or epichlorohydrin process. In other cases, however, integration is not possible; for example, in PO production by means of the CHPO technology, 2.0 tons of $CaCl_2$ (40 tons of wastewater containing the alkali salt) per each ton of PO are obtained as a co-product [54]. The recycling of the solution produced in the dehydrochlorination step to the electrolysis cell of the chloro-alkali facility (the high electricity-consuming process currently used for Cl_2 production) has been considered as a possible option to make the process more sustainable; however, this option has not yet been implemented at an industrial level.

On the other hand, problems might be encountered in the case that HCl returns from isocyanates or epichlorohydrin should outgrow DCE capacity, and if the co-product in the chloro-alkali process of NaCl solution electrolysis, caustic soda, should not find continuing markets, given its predicted lower growth rate. Selling the HCl in the form of concentrated hydrochloric acid is an option, but it is only feasible as long as there is a market for aqueous solutions of hydrochloric acid. Moreover, the economics for selling the acid are also affected by the costs associated with the necessity of demineralized water and technology to eliminate trace organics from the HCl gas.

Integration of chemical processes co-producing HCl with downstream processes is economically feasible by using efficient technologies for HCl transformation to chlorine, and using it, for instance, for chlorination processes (Fig. 2), e.g., for the synthesis of phosgene. This would also allow generation of chlorine without caustic soda co-manufacture. Technologies to convert HCl to chlorine have existed for decades, but have been refined in recent years.

Electrolythic processes, e.g., the current Hoechst–Uhde–Bayer process and the new UhdeNora–Bayer ODC processes are well-established technologies. Recently, Bayer built a 215,000 tpy HCl-to-chlorine electrolysis unit as a part of its massive investments in isocyanate and polycarbonate manufacture in China. Electrolysis is a low temperature operation (70–90 °C) and the amount of water associated with chlorine is lower than with thermochemical processes. Also, the co-produced hydrogen has a commercial value. Until recently, the only available electrolytic recycling process was the Uhde process (nine plants in operation worldwide); anhydrous HCl is first absorbed in water and the resulting aqueous hydrochloric acid solution (22 wt.% HCl) is electrolyzed in a cell to yield chlorine at the anode and hydrogen at the cathode. The energy requirement is approximately 1500 DC kWh per ton of Cl_2 produced. Disadvantages of this technology are (a) a decrease in the current efficiency and corrosion of cell components because of the by-production of some oxygen (the reversible potentials for the evolution of oxygen and chlorine are very close); and (b) the need for a unit for the upstream HCl absorption step and for the drying stages required to remove the 1–2% water associated with the chlorine. These disadvantages have been overcome by the DuPont process, with the direct gas-phase electrolysis of anhydrous HCl to chlorine in a polymer electrolyte membrane fuel cell (PEMFC)-type electrolyser [83]. One benefit achieved is the elimination of the HCl gas absorption step; moreover, if the feed to the anode is anhydrous HCl gas, the water vapour associated with the chlorine produced is minimal, resulting in a simplified downstream separation scheme. The electrolyser can be operated at high current densities then with the liquid-phase electrolysis, which implies a reduction of the size of the electrolyser required for attaining a fixed production of chlorine. In the electrolyser, the anode and the cathode are separated by a Nafion membrane. The primary reactions take place in the thin catalyst layers on the membrane; the latter acts as the electrolyte providing the transport of protons from the anode to the cathode.

The direct decomposition of HCl into H_2 and Cl_2 (thermochemical process) is thermodynamically unfavourable at all practical temperatures. Therefore, thermochemical transformation is possible only if the transformation of HCl is coupled with a thermodynamically favourable reaction. This is the principle of the Deacon catalytic oxidation process, that couples the oxidation of Cl^- and the reduction of oxygen resulting in the formation of chlorine and water. The Deacon process is operated at high temperatures (400–450 °C), catalyzed by Cu chloride, and is limited to 60–80% per pass conversions. There have been three commercial processes based on the Deacon reaction, but using different catalyst systems: (a) the Shell-Chlor, (b) the Kel-Chlor (developed by Kellog), and (c) the MT-Chlor (by Mitsui Toatsu), in a fluidized-bed reactor, that allows a easier removal of the reaction heat. Presently, Mitsui Toatsu is operating a 50,000 tpy plant. Drawbacks of this technology are the high temperature operation, the relatively low single pass conversions and the co-production of water vapour, that necessitates an extensive downstream separation scheme.

However, Sumitomo Chemical has recently developed an innovative titania (rutile)-supported RuO_2 catalyst, offering higher activity than conventional catalysts, rendering it usable at lower temperatures [84]. A fixed bed reactor was developed, accomplished by improving the thermal conductivity of the catalyst, and by dividing the reactor into several zones; each zone is filled with a different kind of catalyst, differing in composition (Ru still remaining the main component of the active phase). A commercial plant using this technology has been operating since 2003. This new technology not only achieves Sustainable Chemistry by chlorine recycling, but also allows for a reduced consumption of resources and energy with respect to salt electrolysis; the chlorine produced is reported to be purer than that obtained by electrolysis of NaCl.

However, new technologies based on oxychlorination (that is, the reaction conducted in the presence of HCl and air, instead of Cl_2) offer the opportunity to use directly co-produced hydrogen chloride for the synthesis of large volume intermediates, i.e., besides DCE, also allyl chloride, chlorinated methanes and phosgene. The substitution of hydrogen chloride for chlorine in the manufacture of these chemicals has the potential of achieving significant savings in manufacturing costs, since it would no longer require units for converting hydrochloric acid into chlorine.

One example is the synthesis of phosgene (current production around 7 million tpy); phosgene is applied for the preparation of polyurethanes and polycarbonates, minor applications being for the synthesis of isocyanates, chloroformates and carbonates. Phosgene is currently produced from the reaction of carbon monoxide with chlorine over an activated charcoal catalyst. The phosgene produced by this process usually contains 400–500 ppm carbon tetrachloride. In 1948 Socony-Vacuum Oil Company invented a method for the production of phosgene from carbon monoxide, hydrogen chloride and air with a $CuCl_2$ catalyst; other companies investigated this reaction [85]. However, several problems prevented this technology from industrial application, amongst which a rapid catalyst deactivation because of volatilisation of the active component. Recently, Bayer and Wacker studied the chemistry of silica-supported $CuCl_2$/KCl catalyst, providing clear evidence for a renewed interest in the chemical industry for this kind of technology [86].

The chemistry of the reactions of oxychlorination and oxyfluorination of hydrocarbons was also the subject of several investigations during the 1970s, and there has been a renewed interest in recent years [87–93]. In catalysts based on $CuCl_2$ supported over alumina, the type of alkaline or alkali earth metal ion dopant greatly affects the catalytic performance, determines the characteristics of the Cu species under steady-state reaction conditions, and finally affects the catalytic performance in terms of both activity and selectivity to the desired compound. Therefore, the redox properties of Cu can be controlled by the choice of the proper type of dopant, eventually optimising the catalyst composition in function of the reaction advancement along the various catalytic beds in multi-layer fixed-bed reactors. Interestingly, the same approach can also be used in the case of the titania-supported vanadium oxide catalyst for *o*-xylene oxidation to phthalic anhydride [9]; in this case the type and amount of alkali metal ion used for catalyst preparation is also changed according to the position of the corresponding catalytic layer in the multi-bed tubular reactor. Hence, the proper design of the catalyst composition may allow optimal performance to be reached, filling the gap that typically makes the oxychlorination of hydrocarbons a less selective reaction than chlorination.

The ultimate solution to decrease the use of chlorine in the chemical industry is to replace chlorinated reactants and intermediates with non-chlorinated compounds. Remarkable examples are the hydroperoxidation routes for epoxides synthesis, that are foreseen to progressively replace the chlorohydrin route for PO manufacture in the future, and the use of carbonates in place of phosgene and other chlorinated compounds. For example, dimethylcarbonate, synthesised by the environmentally friendly oxidative carbonylation of methanol, is an effective methylating agent, that could take the place of methyl chloride or dimethylsulfate; diphenylcarbonate is used in place of phosgene for the reaction with bisphenol A in the Asahi process for the synthesis of polycarbonates [94]. Another option is decrease the number of Cl atoms used for the synthesis of the chlorinated intermediates; for example, in the Epicerol process, recently developed by Solvay [95], glycerol is first made react with HCl to produce glycerol dichlorohydrin isomers, which are then transformed into epichlorohydrin by reaction with NaOH, for an overall input of two Cl atoms (in the form of HCl), and release of one Cl atom (in the form of NaCl). This process has replaced the former three-step synthesis from propene, with intermediate formation of allyl chloride and of glycerol dichlorohydrin isomers, which had an overall input of four Cl atoms (in the form of Cl_2), three of which were finally released in the form of HCl/NaCl. These examples demonstrate that the replacement of halogenated reactants with less toxic compounds, that do not co-produce HCl, does not only meet the criteria of better sustainability, but may also be a more economically viable choice.

4. Conclusions

The chemical industry is experiencing important changes, the driving force for which is the need to improve competitiveness while complying with the regulations aimed at safeguarding human health and the environment. Selective oxidation catalysis plays a fundamental role in this context; indeed, if we consider that oxidation is the tool for the production of huge quantities of intermediates and monomers, it becomes clear that the impact of these productions on the environment might have been much greater than it is if a considerable effort had not been spent on the continuous improvement of the oxidation technologies – by replacing toxic or dangerous reactants, by developing more efficient systems for heat recovery and for energy integration in the plant, and by minimising waste streams. However, a great effort is still needed in order to develop alternative technologies that are more sustainable than traditional ones, while being economically sound at the same time. The examples reported demonstrate that margins exist not only for the improvement of the processes currently in use, but also for rethinking the chemical productions through innovative approaches.

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