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#### Review

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#### A review on catalytic oxidation of chloroaromatics from flue gas

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#### Abstract

Commercial catalysts for the catalytic oxidation of chloroaromatics are mainly based on either noble metals or transition metal oxides supported on a suitable carrier. This paper reviews studies relative to these two generic groups of catalysts and their performances for chloroaromatic decomposition, i.e. conversion efficiency, stability and selectivity towards harmless products (e.g.,  $CO_2$ ), and in particular, avoiding the formation of polychlorinated by-products. The various approaches towards improved catalysts, including tuning the support, adding dopants or promoters, improving the preparation methods, or auxiliary means such as the introduction of ozone ( $O_3$ ) or hydrogen peroxide ( $H_2O_2$ ) in the gas to be treated, and combination with non-thermal plasma treatment are systematically reviewed. This review also appraises various modes of deactivation (i.e., originating from fouling, coking, poisoning, sintering of the catalyst, and from volatilization of its active phases) as well as possible methods for regeneration.

X

Keywords: catalytic oxidation; chloroaromatics; molecular mechanism; catalyst

modification; catalyst deactivation.

#### Acronyms

AC	activated carbon
ADF	Amsterdam Density Functional
CBzs	chlorobenzenes
CNTs	carbon nanotubes
CPhs	chlorophenols
CTAB	cetyltrimethylammonium bromide
DFT	density functional theory
FESEM	Field emission scanning electron microscope
HCBzs	hexa-chlorobenzenes
НОМО	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MAS	Magic Angle Spinning
MSW	municipal solid waste
MSWI	municipal solid waste incineration
NMR	Nuclear Magnetic Resonance
NTP	non-thermal plasma
PAHs	polycyclic aromatic hydrocarbons
PBE	Perdew-Burke-Ernzerhof generalized gradient approximation
PCBs	biphenyls
PCDDs	polychlorinated dibenzo-p-dioxins
PCDFs	polychlorinated dibenzofurans

PICs	Products of Incomplete Combustion
POPs	unintentional Persistent Organic Pollutants
PW91	Perdew–Wang 91 functional
rPBE	revised PBE corrected for the local Lieb–Oxford bound after
	Hammer, Hansen, Nørskov
SCR	selective catalytic reduction
SDDS	Shell dioxin destruction system
SEM	scanning electron microscope
STM	scanning tunneling microscopy
TEM	Transmission Electron Microscope
TOC	total organic carbon
TOF	The turnover frequency
TPD	temperature programmed desorption
TPR	temperature programmed reduction
UV	ultraviolet
VOCs	volatile organic compounds
XPS	X-ray photoelectron spectroscopy

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1. Introduction	

#### **1. Introduction**

#### 1.1. Dioxins and incineration

Polychlorinated dibenzo-p-dioxins (PCDDs), or in brief dioxins, have traditionally been associated with chemical syntheses involving chlorophenols, at times leading to chloracne among personnel [1]. Since their discovery (1977) in the effluents from municipal solid waste incineration (MSWI), however, they are treated together with polychlorinated dibenzofurans (PCDFs), biphenyls (PCBs), and hexa-chlorobenzenes (HCBzs). These compounds are listed and targeted for removal by the Stockholm Convention on Persistent Organic Pollutants (POPs) [2].

Waste incineration and the concomitant recovery of heat commenced already in the  $19^{th}$ century, first in England and later in the USA. On the continent, Hamburg was the first City to adopt this route, following an outbreak of cholera. The development of modern mechanical grate incinerators for eliminating municipal solid waste (MSW) started in the 1930s and attained maturity already in the 1960s and 1970s [3]. The next decades were characterized by the stepwise tightening of emission norms, in particular, relative to grit, dust and associated heavy metals, acid gases (HCl, SO<sub>2</sub>,

HF), as well as trace amounts of Products of Incomplete Combustion (PICs), including chloroaromatics, e.g., PCDDs, PCDFs PCBs, etc. These compounds are semi-volatile and tend to adhere to particles, as well as to deposits settled on boiler pipes and duct walls [3]. Once released to the environment, these semi-volatile compounds are either oxidized photo-chemically in the atmosphere or become associated with particles and deposit. Moreover, they can accumulate in the food chain due to fat-soluble, causing carcinogenic, teratogenic and mutagenic concerns. Hence, many countries implement stringent regulations for incinerator and industrial PCDD/Fs emissions [4-7] considering their low Allowable Daily Intake and high toxicity [1].

Although PCDD/Fs may be generated naturally [8], they mainly form from anthropogenic sources, especially from incineration and other combustion processes [9]. Ever since the discovery of dioxins in the flue gas from MSWI, great efforts were made to try and find their origins, sources, and routes of formation. Complex high temperature gas phase reactions involve PICs that could figure as PCDD/F-precursors, yet the bulk of these PCDD/Fs form only in a temperature window of 200 - 450 °C, following heterogeneous reactions involving flue gas and deposited or entrained fly ash. Accordingly, two major PCDD/Fs forming pathways have been presented and are widely accepted today: these are the *de novo* synthesis and precursor routes. The latter involve substances structurally similar to PCDD/Fs, such as chlorophenols (CPs), chlorobenzenes (CBzs), PCBs, or polycyclic aromatic hydrocarbons (PAHs). Such compounds are easily converted into PCDD/Fs by either condensation of monocyclic precursors or oxidation of polycyclic structures. The *de novo* route refers to the formation from sources of carbon, such as soot arising in oxygen-deficient flames, charred paper or wood, etc. As a first step, it involves the chlorination of such carbon at low temperature, followed by catalytic carbon oxidation, producing mainly carbon

dioxide and monoxide, as well as a variety of *de novo* products, including minute amounts of PCDD/Fs as well as of PCDD/F-precursors.

For many years, CBzs and CPs have been considered as suitable surrogates or PCDD/Fs indicator compounds, present at higher concentrations as well as correlated with PCDD/Fs. Lavric et al. [10] reviewed CBzs and CPs data. Other research proposed 1,2,4-trichlorobenzene with correlation coefficient R<sup>2</sup> 0.97 [11] and 0.89 [12], or 1,2,4,5-tetrachlorobenzene with R<sup>2</sup> 0.80 [13] as surrogates. In addition, CBzs and CPs also exist in MSWI flue gas at higher concentrations. Most are persistent, lipophilic, chemically and thermally stable, toxic, and difficult to decompose entirely; the U.S. EPA lists several CBzs as environmental priority control pollutants [14]. Consequently, much effort has been devoted to the development and testing of treatment methods of PCDD/Fs, PCBs, as well as of a variety of other chlorinated aromatic and aliphatic compounds.

#### 1.2. Treatment techniques for chloroaromatics

Treatment techniques for chloroaromatics have been proposed, tested and developed for eliminating chloroaromatics from various gaseous and aqueous effluents, as well as soil and fly ash. This review is dedicated to only the cleaning of flue gas, or comparable gaseous effluents, and exclusively by catalytic decomposition. Still, there is sufficiently wide offer of catalysts and carriers, and of their improvement and deactivation to justify an analysis and assessment.

Some of these techniques tackling chloro-aromatics merely involve a phase transfer to suitable scrubbing liquors (oils), absorbents (waxes, plastics) and adsorbents (activated carbon, molecular sieves...). Other methods feature thermal, chemical, catalytic, or microbiological treatment, or the use of advanced photo- or physicochemical techniques [15-24].

**Prevention and inhibition or suppression.** In principle, the formation of PCDD/F may be avoided or reduced, by appropriate measures, such as completing the combustion much further and deeper, so that there are much less surviving precursors, avoiding combustion upsets, by more regular feeding of well-mixed materials, or rapid quenching, thus avoiding the temperature window of formation [22]. Inhibition or suppression is based on the injection of sulfur- [25-28], nitrogen- [29-31], or caustic compounds that effectively will suppress formation, presumably by poisoning the dioxins forming catalysts and/or conversion of chlorinated compounds into the corresponding amines, cyanides...[26, 29, 30, 32, 33]

**Phase transfer.** The phase transfer of volatile and semi-volatile compounds engages their transfer and the concentration of minute concentrations of chloroaromatics, to either the bulk of organic liquid or solid phases that are able to dissolve chloroaromatics by absorption, or to the surface of suitable adsorbents (adsorption). Adsorbents feature a large specific surface area and an appropriate micro-porous structure adapted to external and internal transport, and capable of adsorbing and occluding organic pollutants. Currently, activated carbon (AC) is the most widely applied adsorbent [15]. Inorganic adsorbents, such as molecular sieves, are preferred for flue gas systems (e.g., from metallurgical thermal processes) in which the fly ash or filter dust is pyrophoric or otherwise may lead to fires in baghouse filters [16, 17]. However, adsorption only accomplishes a transfer of pollutants from mobile phases to immobile or less mobile ones. The contaminated adsorbent is subsequently regenerated by thermal treatment at temperatures sufficient to destroy the PCDD/Fs or disposed of in an appropriate incineration facility, which represents a sizeable technical and economic cost. Still, it is often used as a pre-treatment, preferably in combination with other treatment methods that ensure the decomposition of the

separated chloroaromatics [18, 34].

Absorption of PCDD/Fs in oil is a patented method that has never been applied industrially. Absorption in plastic materials is strong and reversible (by rising the temperature or reducing gas phase concentration), as experienced during wet scrubbing (memory effects) and in the Adiox<sup>®</sup>-system developed by Forschungszentrum Karlsruhe and marketed by Götaverken. Dioxin molecules in the flue gas are first absorbed by the polymer, then they diffuse to carbon particles where they are bound powerfully to the surface [35, 36].

**Microbiological treatment techniques** can be applied directly to the bioremediation of, e.g., soil contaminated by chloroaromatics. Such treatment is slow and typically leads to incomplete conversion with possibly objectionable intermediates. In addition, only a relatively small number of treatment units are available [19-21].

Also, microbial filters could be used to treat PCDD/Fs in gases, yet these techniques cannot be applied directly to hot gaseous effluents.

**Thermal decomposition and destruction.** Incineration is a conventional technique for converting chloroaromatics into mineral compounds, mainly CO<sub>2</sub>, H<sub>2</sub>O, and HCl. The terms thermal and catalytic combustion apply to gaseous effluents. Still, inevitably, Products of Incomplete Combustion (PICs) also arise. The treatment time in the gas phase usually is stipulated at >2 s and an operating temperature above 850 °C for general waste, to achieve complete conversion of all pollutants present [37]. Nevertheless, problems may arise in case of poor mixing in the flue gas, or following an upset in the upstream combustion conditions. Start-up and (less so) shutdown conditions may lead to a high multiple of PCDD/Fs formation, compared to standard conditions [38].

The elimination of chloroaromatics (or any waste with more than 1 % of halogenated

organic substances) even requires a mandatory temperature of 1100 °C, resulting in extra auxiliary fuel costs [39]. Moreover, incomplete combustion can cause the formation of a variety of harmful by-products.

NO<sub>x</sub> is another by-product of high-temperature combustion [22] and its formation correlates inversely with that of CO and PICs. Incomplete combustion leads to later reformation of PCDD/Fs during cooling, in a temperature window from 500 to 200 °C. Some units use a rapid quench to avoid this occurrence.

**Plasma technique**s produce various active species, radicals and ions, which provide a cascade of chemical reactions, promising high removal efficiencies of chloroaromatics. Non-thermal plasma operates in quasi-ambient conditions but suffers from low energy efficiency, low mineralization degree and a potential generation of pollutants [23].

Photocatalysis is a promising technique that can be applied in numerous and diverse fields, such as antibiosis, deodorization, and water treatment, while featuring low energy consumption, mild reaction conditions and non-selective mineralization of most organic pollutants. When submitted to lighting, semiconductor catalysts generate electron-hole pairs that tend to capture electrons, resulting in strong oxidation abilities. They convert H<sub>2</sub>O adsorbed onto the catalyst surface generating highly active •OH radicals that decompose organic pollutants. Compared with sunlight, ultraviolet (UV) light of wavelength 10 - 400 nm is more beneficial to PCDD/Fs decomposition [40]. Many successful studies have been carried out on the photocatalytic oxidation of dioxins [41-43] stimulated by UV-light, possibly also assisted by O<sub>3</sub> addition [44]. However, photocatalytic oxidation needs long residence times and the by-products formed easily deposit on the active surface, resulting in catalyst deactivation. As with cold plasma, there is also a technical problem in upscaling the method, from

laboratory gas flows (typically <1 m<sup>3</sup>/h) to their industrial counterparts (10,000 to 1 M m<sup>3</sup>/h).

**Catalytic and thermal oxidation**, the focus of the present review, can completely degrade chloroaromatics to harmless (CO<sub>2</sub>, CO, H<sub>2</sub>O) and easily removable combustion products (HCl, Cl<sub>2</sub>). Catalytic units operate typically at temperatures below 500 °C and thus cost less in auxiliary fuel than thermal units. Conversely, catalysts remain expensive and subject to deactivation by various mechanisms such as coking, poisoning or – in the case of a temperature runaway – sintering [45]. Such a reaction runaway occurs in case temperature rises faster than the spontaneous or organized cooling of the reactor can cope with.

This review centers on current state of the art techniques and on the technical challenges remaining, related to this remediation technology. Several interesting reviews have been published, each of these examining different aspects of the title subject. Everaert and Baeyens[46] proposed a general review on catalytic oxidation, yet they do not cover chloroaromatics specifically. Recently, their work was complemented by Huang et al. [47], with their focus on low temperature processes. In their review paper, Aranzabal et al. [48] covered the abatement of chlorinated volatile organic compounds (VOCs, such as chlorobenzenes, trichloroethylene, or dichloromethane) but omitting PCDD/Fs from their scope. Other reviews specifically emphasized industrial installations and processes [49, 50].

#### 1.3. Scope of this study

Expanding on these earlier review studies, this paper provides systematic, comprehensive overviews of all catalysts and catalytic processes tested and dedicated to decompose chloroaromatics, covering both academic developments and their industrial realization. Doing so, it considers all aspects of catalysis science, starting

from catalyst preparation and adaptation, over relevant processes and their operation, to catalyst deactivation and regeneration, and finally catalytic reaction mechanisms and their significance with respect to stability, selectivity and activity. In this paper, "removal" is defined as that the pollutants disappear from the gas, yet their molecules may be either totally or partially destroyed or remaining intact, their removal resulting from adsorption onto the catalyst; "decomposition" or "degradation" infers that the pollutants are converted into smaller yet still organic molecules; "destruction" means that the molecules of the pollutants are completely destroyed, in the case of chloroaromatic oxidation, to CO, CO<sub>2</sub>, H<sub>2</sub>O, HCl, Cl<sub>2</sub>, etc.

#### 2. Industrial installations for eliminating dioxins

Currently, PCDD/Fs can be removed from flue gas by the following functions or principles:

- Adsorption, on activated carbon [51-53], molecular sieves, or other adsorbents,
- Catalytic decomposition in honeycomb monolith reactors [54] or in packed bed reactors, such as in the Shell dioxin destruction system (SDDS) [55, 56],
- Combined filtration and decomposition in a catalytic filter [57-60],
- Wet or semi-dry scrubbing achieves a partial removal of PCDD/Fs [54].
- Adiox system [35].

#### 2.1. AC adsorption

Adsorption on AC is the most widely used method for end-tail emission control of PCDD/Fs and in a majority of cases it meets the limit value successfully. The first process to be used featured fixed bed adsorption: the bed temperature as well as carbon monoxide in the effluent gas was monitored, to detect timely a possible bed ignition. Moreover, after a prolonged operating period, probably of more than a year a breakthrough is in principle possible; still, the dioxin retaining capacity seems

somewhat ill-defined.

Later, it was discovered that the injection of AC followed by its separation in a filter allowed to eliminate dioxin safely, with only very limited investment, covering an AC-hopper and feeding system, e.g. a screw conveyer and a chute, leading the AC into the flue gas duct. Testing showed that the distribution of AC should cover the entire duct section and that the first meters of joint travel (of AC + flue gas) are much more effective than to expand this distance over great length. Supplemental adsorption takes place while the flue gas percolates through the filter cake, retained on baghouse filter sleeves. Thus, the baghouse filter scored better than the Electrostatic Precipitator or the cyclone dust collector.

The effect of operating parameters on the adsorption was studied methodically and presented graphically by Lu et al. [61].

Some early adsorption systems used mineral adsorbents, such as Molecular Sieves, or Minsorb<sup>®</sup>. Since their efficiency is markedly lower, they are mainly used in metallurgical applications, to avoid the ignition of mixes of pyrophoric dust with AC. As stated already in Section 1.2, this adsorption method only transfers the burden of dioxins to further fly ash treatment. At times, this method even can cause additional dioxin formation [62].

#### 2.2. SCR

The Selective Catalytic Reduction (SCR) system is widely used for reducing NO<sub>x</sub> to  $N_2$  (deNO<sub>x</sub>); also, some  $N_2O$  is formed. In MSWI it is increasingly applied for additional PCDD/Fs removal, since SCR catalysts effectively eliminate chloroaromatics in a temperature range similar as for the SCR process [54, 63]. The flue gas is reheated to 220-400 °C and led into a catalytic tower, equipped with catalytic honeycomb monoliths.



Figure 1. Process flow diagram of the deNO $_x$  at the MSWI of Ghent. [64]

Kim et al. [65] and Wang et al. [63] both found good performances of such SCR systems for decomposing PCDD/Fs in the flue gas from different municipal solid waste incinerators. The elimination efficiency of baghouse filtration (it removes solid phase PCDD/Fs) combined with SCR unit (it removes gas-phase PCDD/Fs) can reach as high as 99.1% [54]. According to Goemans et al. [64], 99% of PCDD/Fs and 90% of NO<sub>x</sub> were removed simultaneously at the MSWI of Ghent, Belgium (Figure 1). This system requires only minimal additional investment (a supplemental layer of catalyst) when it is retrofitted to an existing deNO<sub>x</sub> unit [49].

An important consideration is the presence of  $SO_2$  in the flue gas, since a higher operating temperature is required in its presence, in order to avoid the forming of solid salts of ammonium sulfate that gradually obstruct the catalytic bed. Complete regeneration is possible, however, by reheating the catalytic bed, thermally decomposing the deposited salts.

#### 2.3. SDDS

In the 1990's Shell introduced the SDDS, featuring a highly reactive dioxin decomposition catalyst, which effectively degrades PCDD/Fs, PCBs, PAHs, etc. [49, 55]. This SDDS comprises a lateral flow reactor and VO<sub>x</sub>/TiO<sub>2</sub> extrudates, used as catalyst. The granular catalyst and the flexible design of the lateral flow reactor make the system easy to install or retrofit into existing housing and also allow low-temperature oxidation. According to the producers, at 220 °C in waste incinerators the system achieves at least 85% removal efficiency of PCDD/Fs [66]. Liljelind et al. [55] investigated the PCDD/Fs removal ability of a SDDS unit, using a lab-scale incinerator. The removal efficiency reached even >98% at 150 °C.

#### 2.4. Remedia

The REMEDIA<sup>®</sup> D/F Catalytic Filter System was developed by W.L. GORE & Associates GmbH in 1998. The system integrates dust elimination and catalytic decomposition. Dust in the flue gas is filtered by a polytetrafluoroethylene membrane incorporating the catalytic particles that decompose the trace amounts of organic chlorinated pollutants into carbon dioxide, water and hydrogen chloride. Compared with a separately operating baghouse filter and catalytic reactor, the concentration of solid-phase PCDD/Fs in fly ashes of catalytic filter is much lower [60]. Many MSWI plants install this system and successfully reach the limit values for PCDD/Fs. Syc et al. [57] reported flue gas emission data from the municipal solid waste incineration plant Termizo a.s. in Liberec (Czech Republic), equipped with electrostatic precipitator, REMEDIA® D/F Catalytic Filter System and a three-stage flue gas scrubber. The catalytic performance of this system remained stable even after 1,5000 hours of operation and the PCDD/F stack emissions amounted to 0.013 - 0.031 ng TEQ/Nm<sup>3</sup>, i.e., 3 to 8 times lower than the Czech and E.U. emission limit (0.1 ng

TEQ/Nm<sup>3</sup>). Hung et al. [67] used a catalytic filter system to deal with waste gas from MSW-fueled stoves and according to their study, at 210 °C, the removal efficiency of chlorobenzenes and chlorophenols attained 89 and 88 %, respectively.

#### 2.5. Summary

In most industrial countries, the emission standards of dioxins from MSWI flue gas can be respected using existing techniques; the most widespread techniques are adsorption on activated carbon (AC) and catalytic conversion using SCR-catalysts. The same type of catalyst ( $V_2O_5/TiO_2$ , often modified by adding WO\_3 or MoO\_3), effectively decomposes dioxins [68-70] at a temperature typically of 200 - 300 °C. However, the usual flue gas temperature after the baghouse-filter is 140 - 170 °C. Therefore, extra energy is often required to reheat the flue gas to 200 - 300 °C. Also, PCDD/Fs are formed in the cooling sections (boiler, gas cleaning) of the incineration plant [71, 72], aided by the catalytic action of fly ash containing metal chlorides [73] and oxides. The same could happen during reheating. To avoid possible extra energy consumption and dioxin formation, novel catalysts should be developed with effective catalytic activity at low temperature ( $\leq 150$  °C), or assisted with auxiliary methods (e.g. O<sub>3</sub> introduction)

In addition, many plants are averse to install catalytic systems due to high operating and maintenance cost. Globally, most MSWI plants still use AC adsorption, combined with baghouse-filtration to remove dioxins from flue gas, although operating often under huge pressure from more stringent MSWI emission standards, particularly in China. Therefore, studies are meant to lower the overall cost of the catalytic system by lowering its operation temperature, prolonging guaranteed lifetime, developing in situ regeneration techniques to decrease replacement cost and finally, finding alternative highly effective catalysts which are cheaper and environmentally friendly.

#### 3. Catalytic oxidation

The commercial catalysts used for the catalytic oxidation of chloroaromatics are based either on noble metals (3.1) or on supported transition metal oxides (3.2). Their reaction mechanism is discussed in this section 3. The next sections 4 and 5 are devoted to the preparation, activity, selectivity, stability and further improvement of catalysts.

#### 3.1. Supported noble metal-based catalysts

There are only few reports dealing directly with the mechanisms of catalytic decomposition of chloroaromatics on noble metal-based catalysts. At room temperature and due to the strong interaction of Cl with noble metals, some dissociative adsorption of chlorobenzene could be observed on a Pd(111) surface, accompanied by C-Cl bond scission [74]. Hydrogen-deuterium isotope exchange allowed to study how C-H bond scission affects the oxidation of chlorobenzene on  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and revealed that the phenyl group not easily reacted further, following the poisoning of active sites by chlorine produced from the dissociative adsorption of chlorobenzene [75]. When at more elevated temperature this chlorine was again removed (partly by reacting with adsorbed phenyl rings to form polychlorinated benzenes), further oxidation of phenyl would again occur.

#### **3.2. Supported transition metal oxides**

**Reaction steps.** The catalytic decomposition of chloroaromatics over transition metal oxides comprises two key steps, as shown in Figure 2.

The first step is the dissociative adsorption of chloroaromatics onto the catalytic surface, forming surface phenolate structures via Cl abstraction [76-81]. During adsorption, the benzene ring remains intact, as observed during *in situ* FTIR spectroscopic studies [76, 82-84]: all species detected after adsorption of

chloroaromatics onto the support were ring structures indeed. For most of the catalysts studied, the dissociative adsorption of the C-Cl bond is not the rate limiting step since it is fast: after few minutes of oxidation no peaks corresponding to C-Cl vibrations could be perceived any more. However, also polychlorinated- and polyaromatic compounds such as dibenzofurans adsorb through their oxygen atom[79, 85].

In a second step, proceeding at sufficiently elevated temperature, the partially dechlorinated substances may be subject to electrophilic substitution while adsorbed onto the catalytic surface. This step may form o-benzoquinone, p-benzoquinone, or result in nonaromatic species, as observed spectroscopically [76]. These species are also oxidized further, forming surface maleates and carboxylates such as acetates and formates. These phenolates, benzoquinones, or carboxylates are relatively easily oxidized, compared to maleates. In particular, carboxylates are easily oxidized by gaseous oxygen [58,59,172], at a rate almost one order of magnitude higher than the relatively stable maleates [59].



Figure 2. Reaction mechanism for the oxidation of chlorinated benzenes V2O5/TiO2 catalysts. [76]

The role of oxygen species (i.e., gaseous oxygen, surface chemisorbed oxygen, and lattice oxygen) has been widely investigated. When no oxygen is introduced, still some partial oxidation products (maleic acid, acid salts, etc.) can be found on the catalyst surface, proving thereby that some surface lattice oxygen operates actively during oxidation (cf. the Mars and van Krevelen mechanism) [76, 81, 86].

Gaseous oxygen can later replenish the missing lattice oxygen at the catalytic surface, reacting at the same time with intermediates to form CO,  $CO_2$  and  $H_2O$  and - at large enhancing oxidation rates [82-84, 87]. However, the replenishment of lattice oxygen or re-oxidation of vanadium oxide by gaseous  $O_2$  is probably limited by its intrinsic oxidation ability, since it is generally observed that the V oxidation state to some

extent decreases during catalytic oxidation, even when using high  $O_2$  levels (> 10%~11%). Thus, especially at low space velocity excess oxygen is superfluous [87-90].

**Reaction order.** The reaction order relates the influence of the reactants concentration on the catalytic rate. It has been studied extensively for different reactions and similar values were found for both chloroaromatics and O<sub>2</sub> [83, 84, 91, 92]: in all cases the reaction order in chloroaromatics was approximately unity, while with respect to oxygen it was observed to be close to zero, under typical conditions of excess oxygen [76, 83, 84, 91-93]. On the basis of partial reaction order and analysis of intermediates and products, the Mars and van Krevelen mechanism has often been proposed for chloroaromatics [76, 79, 82, 94-96], i.e. an oxidation-reduction mechanism, involving the reaction of a chloroaromatic molecule with oxygen provided by the catalyst, followed by replenishment of the oxygen vacancies in the catalyst with gaseous oxygen.

#### 4. Catalysts

The principal parts in preparing catalysts appropriate for further use in catalytic oxidation are their design, development, and testing. Generally, both the adsorption of chloroaromatics and their consecutive oxidation affect catalytic decomposition. Adsorption mainly relies on surface area, porosity, and availability of surface acid sites, while oxidation is influenced by the redox-ability of catalysts, as estimated by H<sub>2</sub> temperature programmed reduction (TPR) and O<sub>2</sub> temperature programmed desorption (TPD) methods. Generally, the redox-ability of catalysts is related to the number of active sites (dispersion), the valence of active phases and the mobility of oxygen species (usually evaluated by the concentration of surface chemisorbed oxygen which originates from dissociative adsorption of gaseous oxygen on surface

oxygen vacancies of the catalyst [97-99]).

Improved and novel catalysts, showing high catalytic activity already at low temperature (< 150 °C), are essential to avoid extra energy consumption required for reaching reaction temperature and dioxin formation. Besides, catalyst stability and the selectivity of conversion towards stable final products (CO<sub>2</sub>, H<sub>2</sub>O, HCl) are to be taken into account.

Table 1 considers the catalyst formulations reported to abate chloroaromatic compounds.

#### Table 1. Survey of catalyst formulations used to oxidize and abate

chloroaromatics.

Pollutant	Catalyst	Reference
Monochlorobenzene	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	[70, 100-104]
	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -CNTs	[105]
	VO <sub>x</sub> /CeO <sub>2</sub>	[106]
	$MnO_x/TiO_2-Al_2O_3$	[94, 107]
	MnO <sub>x</sub> /TiO <sub>2</sub> -CNTs	[108]
	$MnO_x/TiO_2$	[109, 110]
	MnO <sub>x</sub> /SiO <sub>2</sub>	[111]
	MnO <sub>x</sub> /CeO <sub>2</sub>	[112]
	$MnO_x$ , $O_3$	[113]
	$CuO_x, O_3$	[114]
	Mn-Ce-O	[115]
	Mn-Ce-O/TiO <sub>2</sub>	[115-120]
	Ru-Ce-O/TiO <sub>2</sub>	[96, 121-123]
	Mn-Ce-O/H-ZSM5 (with an appropriate Si/Al	[124]
	ratio at 30)	
	Mn-Ce-La-O	[119]
	Cr-Ce-O/ titanium pillared clays	[125]
	M-Ce-O (M = Co, Cu, Fe, Zr, V, Cr, Ni)/TiO <sub>2</sub>	[126, 127]
	Co-Mn-Ce-O//cordierite	[128]
	Fe <sub>2</sub> O <sub>3</sub>	[129]
	$Fe_2O_3, O_3$	[130]
	Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	[131]
	CuO/CNTs	[114]
	$Pt(Pd)/\gamma$ - $Al_2O_3$	[24, 75, 132-134]
	Pt(Pd)/alumina pillared clays	[135]
	Pt/HFAU (featuring a Si/Al framework ratio of 5)	[136]

	$Pt(Au)/CeO_2$ - $ZrO_2$	[137]
	$Pd/M_3AlO (M = Mg, Co, Ni, Cu, Zn)$	[138]
	Ru/CeO <sub>2</sub>	[96, 121]
	Ru/TiO <sub>2</sub> -CeO <sub>2</sub>	[122]
	$ABO_3$ (A: La, B = Co, Mn)	[139]
Dichlorobenzene	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	[76, 82, 84, 93, 100,
		140-146]
	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SiO <sub>2</sub>	[146]
	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -CNTs	[147]
	$V_2O_5$ -Mo $O_x$ (WO <sub>x</sub> )/Ti $O_2$	[68, 140, 148]
	V <sub>2</sub> O <sub>5</sub> -WO <sub>x</sub> /TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	[91]
	$MnO_x/TiO_2-Al_2O_3$	[107]
	MnO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	[149]
	Mn-Ce-Fe-O	[150]
	Ce-Ti-O	[151]
	Fe <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub>	[152]
	Fe-Ti-O	[153]
	CaCO <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>	[154]
	$Co_r Mn_v O$ (spinel structure)	[155]
	CuO <sub>y</sub> /TiO <sub>2</sub> -CNTs	[90]
	Pt/zeolite	[156]
	YCrO <sub>3</sub>	[157]
Polychlorobenzenes	$V_2 O_5/TiO_2$	[158]
i oryentor obenzenes	$V_2O_5$ - $WO_2/TiO_2$	[89 92]
	$L_{2}O_{2}$ (MgO CaO BaO La <sub>2</sub> O <sub>2</sub> CeO <sub>2</sub>	[159]
	$MnO_2$ , Fe <sub>2</sub> O <sub>2</sub> , and Co <sub>2</sub> O <sub>4</sub> )/Al <sub>2</sub> O <sub>3</sub>	[157]
	$C_{03}O_4$ -CeO <sub>2</sub>	[160]
	Fe <sub>2</sub> Q <sub>3</sub>	[161]
	Fe <sub>2</sub> O <sub>2</sub> -CeO <sub>2</sub>	[162]
	$MO/Fe_{o}$ (M = Mg. Ca. Sr. Ba)	[95, 163]
	$CuO/Mn_{s}O_{s}$	[164]
	$\gamma$ -Al <sub>2</sub> O <sub>2</sub>	[165_166]
	$\int 2\Omega/\alpha$ -Fe <sub>2</sub> O <sub>2</sub>	[167, 168]
	Ph	[169]
	$XY_2O_4(X - Mg C_2 C_1 Ni Z_1 and Y - A)$	[170]
	Fe)	[170]
	$Cu_{x}Mg_{1,x}Al_{2}O_{4}$	[171]
PCDD/Fs	$V_2O_5$ -TiO <sub>2</sub>	[172-175]
TODITS	$V_2O_5/TiO_2$ -CNTs	[176]
	$V_2O_5$ -WO <sub>2</sub> (or MoO <sub>2</sub> )/TiO <sub>2</sub>	[54 174 177-179]
	$V_2O_3 - WO_3/(c) HOO_3/(FO_2)$	[172]
	V <sub>2</sub> O <sub>5</sub> -WO <sub>2</sub>	[1,2]
	$V_2O_3 - WO_3$ $V_2O_2 - C_2O_2/T_1O_2$	[180]
	$V_2O_5 = C_2O_2/11O_2$	[101, 102] [183]
	$v_{2}O_{5}-CCO_{2}/11O_{2}, O_{3}$	[103] [104 10 <b>5</b> ]
	$\Gamma \sigma_2 O_3 (WIIIO_x), O_3$	[104, 103] [196]
DOD	$\mathbf{P}\mathbf{U}/\mathbf{A}\mathbf{I}_{2}\mathbf{U}_{3}$	[100]
PCBs	$v_2 O_5 - W O_3 / T_1 O_2$	[187]
	Fe/Ac	[188]
	$N_1Fe_2O_4$	[189]

#### Chlorophenols

 $Au/Fe_2O_3\text{-}Pt/SnO_2\text{-}Ir/La_2O_3$ 

[190]

#### 4.1. Supported noble metal catalysts

Supported noble metal catalysts tend to perform well while oxidizing VOCs, especially formaldehyde [34]. This class of catalysts comprises mainly platinum and palladium and presents excellent reactivity for decomposing chloroaromatics. However, several shortcomings severely limit their industrial application: their price; their low resistance to chloride poisoning, because of strong interactions between noble metal and chlorine, forming various chloride species [134, 191, 192]; their easy sintering at elevated temperature [52, 136, 193]; generating polychlorinated compounds during catalytic oxidation reactions [21, 52, 194].



a function of Pt-particle size (calculated from CO chemisorption). [195]

The reactivity of noble metal sites is strongly related to their particle size and valence state, apart from their intrinsic properties, support and catalyst preparation method. The turnover frequency (TOF = number of molecules converted per active surface site

and per second [196]) of formaldehyde oxidized over Pt/TiO<sub>2</sub> varied linearly with the size of Pt nanoparticles, as long as this size remained < 10 nm (Figure 3): also the number of Pt nanoparticles on (100) and (111) crystal facets (active sites) and the concentration of chemisorbed oxygen rises [195], explaining the enhanced reactivity. Moreover, the strength of the surface Pt–O bond declines with rising Pt particle size (1.54~10.1 nm), resulting in easier adsorption and desorption of oxygen [197]. However, larger particles (22.3 nm) show lower activity since the Pt surface area becomes smaller, relative to its amount. A similar size-effect was also observed during the oxidation of chloroaromatics, regarding the conversion efficiency of chloroaromatics and the selectivity of polychlorinated by-products [135]. In addition, catalysts with noble metal species of zero valence state exhibit better performances, due to the stronger ability for oxygen activation [198-202]. Therefore, a pre-reduction of noble metal based catalysts is preferred, before the reaction is started. An important problem during the catalytic decomposition of chloroaromatics on noble metal based catalysts is the formation of polychlorinated by-products (mainly higher chlorinated benzenes). This has been widely studied, since polychlorinated by-products are sometimes even more toxic and persistent than the starting pollutant to be oxidized. Many researchers reported that through their (oxy-)chlorides noble metal species are responsible for further chlorination of adsorbed (chloro)benzene species [192, 201, 203, 204]. Chlorination occurs via consecutive electrophilic substitution on the aromatic ring by chlorine or by isomerization reactions [21, 52].

#### **4.1.1. Supported Pt-based catalysts**

The selectivity of supported Pt catalysts to form polychlorinated by-products is strongly influenced by oxygen concentration [24, 192, 205]. The creation of polychlorinated benzenes decreases rapidly with reducing oxygen concentration [192].

This is because oxygen causes surface oxidation of Pt particles to Pt (IV) species (comprising Pt oxides and oxychlorides); these are less efficient in oxidation but more active in chlorination.

In addition, co-feeding of hydrocarbons reduces the formation of polychlorinated by-products and accelerates their decomposition [75, 132, 133, 205]. Various explanations are advanced: (1) Additional heat production during combustion and/or the formation of specific intermediates (e.g. water), accelerate the catalytic oxidation of chloroaromatics [132, 133]. (2) Hydrocarbons reduce Pt to its zero-valent state, the most active Pt-species [132]. (3) Hydrocarbons can react with Cl (forming mainly HCl) adsorbed on the catalyst surface, preventing the formation of Pt-oxychlorides [132]. (3) The removal of Cl from the surface also enhances catalytic reactivity by avoiding the blocking of active sites [75, 132, 133, 205].

Scire et al. [203, 206] and Taralunga et al. [136] reported higher activity for chlorobenzene oxidation with lower production of polychlorinated by-products for Pt supported on zeolite than for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>: the zeolite induced a shape selectivity effect and smaller zeolite channels hampered further chlorination of already chlorinated species. Taralunga et al. [136] analyzed surface reactions on different platinum species (Pt<sup>0</sup>, Pt<sup>4+</sup>) supported on HFAU zeolite (featuring a Si/Al framework ratio of 5) with addition of water vapor and oxygen. The decomposition of chlorobenzene and the generation of polychlorinated benzenes (by-products) with a low amount of Pt<sup>0</sup> can be summarized as follows:

$$C_{6}H_{5}Cl + 7 O_{2} \xrightarrow{Pt/HFAU} 6 CO_{2} + HCl + 2H_{2}O (1)$$

$$2 C_{6}H_{5}Cl + H_{2}O \xrightarrow{PtO_{2}} 2 C_{6}H_{6} + O_{2} + PtOCl_{2} (2)$$

$$PtOCl_{2} \xrightarrow{H_{2}O,O_{2}} PtO_{2} + HCl (3)$$

$$2 C_{6}H_{6} + 15 O_{2} \xrightarrow{PtO_{2}} 12 CO_{2} + 6H_{2}O (4)$$

Equation (1) is the overall oxidation reaction and equations (2 and 3) appear as secondary reactions. On Pt/HFAU catalysts with a large load of  $Pt^0$ ,  $C_6H_5Cl$  reacts with H<sub>2</sub>O, producing  $C_6H_6$  and  $PtCl_4$ . The resulting  $C_6H_6$  is further oxidized to  $CO_2$ and H<sub>2</sub>O, while PtCl<sub>4</sub> chlorinates  $C_6H_5Cl$  to produce  $C_6H_4Cl_2$ .

#### 4.1.2. Supported Pd-based catalysts

Pd is less expensive than Pt and generally more active in the catalytic oxidation of methane, yet it performs less in the oxidation of chloroaromatics [24, 134, 135]. Giraudon et al. [201, 204, 207, 208] studied Pd, supported on hierarchical macro-mesoporous TiO<sub>2</sub>,  $ZrO_2$  and  $ZrO_2$ -TiO<sub>2</sub>. A higher activity was reported for Pd/TiO<sub>2</sub> and attributed to the better reducibility of TiO<sub>2</sub> support (Ti<sup>4+</sup> to Ti<sup>3+</sup>). Complete conversion of chlorobenzene was achieved at 380 °C. The same research group suggested that Pd might not participate directly in the oxidation reaction as there were no obvious relations between Pd dispersion and activity. Thus a two-step reaction scheme was proposed [204]: firstly, chlorobenzene is oxidized by oxygen species supplied by  $Ti^{4+}$  which thus transformed to  $Ti^{3+}$ ; secondly, previously dissociated oxygen species, present on the Pd sites, re-oxidize the  $Ti^{3+}$  to  $Ti^{4+}$ . In this scheme, Pd species seem to control the mobility of oxygen species, while reacting with  $O_2$  to form active  $Pd^{2+}O^{2-}$  [207] and thus refill the oxygen vacancies, thereby closing a Mars and van Krevelen cycle. Besides, polychlorinated by-products are detected during the experiments and the acidity of support seems to decrease the selectivity for forming polychlorinated by-products [208]. The same group also reported the oxidation of chlorobenzene on Pd/perovskites (LaMnO<sub>3</sub>, LaFeO<sub>3</sub>, LaCoO<sub>3</sub>, and LaNiO<sub>3</sub>), with LaFeO<sub>3</sub> performing best. The catalyst was pre-reduced and all Pd species were reduced to Pd<sup>0</sup> species. Pre-reduced Pd supported catalyst showed higher activity indeed [201].

Considering the possible deactivation of catalysts whose active sites are blocked by chlorine, a protonated Pd/Y-zeolite was prepared to study its development during the decomposition of chlorobenzene. With the introduction of protons, an excellent activity was obtained for chlorobenzene oxidation. The formation of polychlorinated by-products was eliminated after relatively short running times and only traces were detected after about 18 h. Introducing protons into the zeolite lattice accelerated HCl formation, thus suppressing the chlorination of organics. In addition, m-xylene was co-fed with chlorobenzene to see whether introducing additional hydrogen had a similar effect. However, the results were not clear-cut, indicating that lattice protons could not be replenished by such methods. [209]

#### 4.2. Transition metal oxide-based catalysts

Transition metal oxide-based catalysts typically use one or more transition metal oxides as active phases; these are finely dispersed on supports such as TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. The surface structures appear related to the concentration of the active component and to the nature of the catalyst carrier. Their interface bonds are generally very strong and they constitute unusual nanostructures (for example, a monolayer or sub-monolayer of VO<sub>x</sub>) since the oxygen atoms of the carrier tend to incorporate into the active phases. These interfaces are usually special sites where reactions can easily occur [210]. Moreover, the charge transfer between active oxides and a reducible support (i.e. TiO<sub>2</sub> and CeO<sub>2</sub>) seems beneficial to enhance the reactivity of a catalyst [211, 212]. Mainly because of its strong interaction with chlorine, however, CeO<sub>2</sub> is rarely applied as support in the catalytic conversion of chloroaromatics. Bertinchamps et al. [69] confirmed that most active phases dispersed better on TiO<sub>2</sub> surface than on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surface and showed superior performances.

The lowest unoccupied molecular orbital (LUMO) energy, the hydrogenation energy and the highest occupied molecular orbital (HOMO) energy of the reduced state were calculated to evaluate the catalyst surface acidity, the oxidizing ability and the re-oxidizing ability, respectively. According to these computational results, three categories of transition metal oxides can be distinguished: those acting as "active

phase" (zone A), "promoter" (Zone B), and "inactive phase" (Zone C) (Figure 4).

Because of its wide application, the data of vanadium oxide is set as reference. [213]



Figure 4a: Hydrogenation energies  $E_{hydrogenation}$  and their relationship with the corresponding LUMO energies  $E_{LUMO}$ . b: LUMO energies of the oxidized state and HOMO energies of the reduced state of oxides in "Zone A of a. Black solid symbols represent the LUMO energy of the oxidized state, blue hollow symbols show the HOMO energy of the reduced state. [213] Copyright 2014 ACS Publications.

Figure 4b shows that the HOMO-energies of reduced  $Cu^{2+}O_x$ ,  $Mn^{4+}O_x$ ,  $Ru^{4+}O_x$ , and  $Rh^{4+}O_x$  come close to that of reduced  $V^{5+}O_x$ , signifying that these oxides possess competitive re-oxidation ability, just as vanadium oxide does. Based on their relatively high acidity, the oxides from "Zone B" of Figure 4a (Mo, Sb, Nb, W, Zn) can be proposed to increase catalyst acidity, especially during the catalytic oxidation of light chloroaromatics. However, also the interaction between "promoters" and main

active phases should be taken into account, in case both are doped in the catalyst: "promoters" with strong basicity (electron donors) can poison active phases (electron acceptors) by providing electrons [213]. After accepting electrons from these dopes, the oxidability of the active phase drops and the catalyst deactivates. Supported transition metal oxides are available at low cost and already active at relatively low temperature (200 - 300 °C); still, some formulations will deactivate when chlorine is present. Typically, they do not generate by-products with higher chlorination degree [22, 140, 214, 215], an advantage over noble metal catalysts.

#### 4.2.1. Supported VO<sub>x</sub>-based Catalysts

Industrial VO<sub>x</sub>-based catalysts are originally applied in the production of sulfuric acid, oxidizing sulfur dioxide to trioxide. Later such catalysts were also used for controlling NO<sub>x</sub> emissions, via its selective reduction using suitable reducing agents, generally NH<sub>3</sub> or urea. Most of the catalysts are based on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>(MoO<sub>3</sub>)/TiO<sub>2</sub> (anatase). Typically, the vanadium content is normally low (< 1 wt.%) to restrict the generation of N<sub>2</sub>O and side reaction of SO<sub>2</sub> oxidation [216]. More recently, they were designated in both laboratory and field studies [217, 218] as stable and active catalysts, suitable for oxidizing chloroaromatics.

Similar surface vanadium oxides (i.e. isolated, dimerized, polymerized, or crystalline species) are generally present on all catalytic surfaces, independently of the nature of the support [219]. However, their relative concentration varies somewhat with the specific support and with its surface coverage of metal oxides.

Extensive studies of supported  $VO_x$ -based catalysts allow to elucidate the structure of surface vanadium oxides and their specific action in the catalytic process. At low coverage vanadia is primarily present as isolated tetrahedrally coordinated vanadyl surface species. At higher coverage, dimeric or polymeric vanadyl species are formed.

Lastly, crystalline species grow onto the surface, when their loading exceeds a monolayer. Raman spectroscopy shows isolated tetrahedrally coordinated surface vanadyl species at about 1030 cm<sup>-1</sup> and dimeric or polymeric vanadyl species at 930 cm<sup>-1</sup> [220], whereas the superior spectral resolution of Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) allows to observe even more vanadyl species [221].

The loading of vanadium on  $TiO_2$  evidently affects catalytic activity and selectivity of the system (Figure 5) [222]. With mounting V-loading, the catalytic activity also augments, reaching a maximum value for ca. 4.5 wt.% of vanadium. Further raising the V-loading tends to deactivate the catalyst. However, growing the V-loading from 1.8 to 5 wt.% causes the CO<sub>2</sub> selectivity to drop, suggesting a different reactivity of various vanadia species.



Figure 5. (a) Temperature for reaching 80% 1,2-dichlorobenzene conversion ( $\blacksquare$ ) and CO<sub>x</sub> selectivity ( $\blacktriangle$ ) at this 80% conversion level, as a function of the theoretical VO<sub>x</sub> density for TiO<sub>2</sub>/WO<sub>3</sub> based catalysts. (b) Product selectivity for samples of different vanadium content. V<sub>2</sub>O<sub>5</sub> = 1.8 wt.% ( $\bigstar$ ), V<sub>2</sub>O<sub>5</sub> = 3 wt.% ( $\blacklozenge$ ) and V<sub>2</sub>O<sub>5</sub> = 5 wt.% ( $\diamondsuit$ ) (CO<sub>x</sub> solid line; dichloromaleic anhydride dotted line). [222]

The most active sites contain vanadium in its highest oxidation state  $V^{5+}$  and surface V-sites undergo a redox cycle,  $V^{5+} / V^{4+}$  in oxidation reactions. Both in its low and high oxidation states, vanadia exhibits strong tendencies to form polymeric species (of

the  $V_2O_3$  or  $V_2O_5$  type) on the TiO<sub>2</sub> surface; their structures easily undergo reduction and re-oxidation by altering the local stoichiometry [223, 224].

Although CO and CO<sub>2</sub> were suggested to be the only carbon-containing products, several authors still found partial oxidized products with or without other pollutants co-feeding in investigations on V-based catalysts. Lichtenberger and Amiridis [141] found a gradual deactivation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst when co-feeding meta-dichlorobenzene with methyl-naphthalene (mNpht), a known coke precursor. Indeed, mNpht accumulated on the catalyst's surface, blocking the active sites. The deactivation was more pronounced at lower temperatures and was fully reversible by oxidation in a O<sub>2</sub>/He stream at elevated temperature. Dichloromaleic anhydride was detected by Albonetti et al. [148, 225]. The presence of tungsten and a certain amount of vanadium resulting in numerous Brønsted acid sites favored the formation of this partially oxidized product, yet this tendency lessened again at elevated temperature. In addition, among transition metal oxide catalysts the selectivity to CO<sub>2</sub> of V-based catalysts is not outstanding [82, 115, 226, 227]. Ce-based catalysts show 99.5% selectivity to CO<sub>2</sub> [115, 226] and CrO<sub>x</sub>/TiO<sub>2</sub> attain about 90% [82]. Since a high catalytic activity is observed in the control of both  $NO_x$  and chloroaromatics involving the most toxic PCDD/Fs, V-based catalysts attract attention more extensively, compared with other transition metal oxides. Lots of fundamental studies have been prepared, to investigate the oxidation mechanisms of chloroaromatics on V-based catalysts, including the role of vanadyl species and the acid sites. These are discussed in the following sections.

#### **4.2.1.1.** The role of different vanadyl species

Although the detailed molecular structure of active sites is still a source of discussion, there is no doubt that these three functional groups V=O, V-O-V, and V-O-Ti are the

main components of active sites in  $VO_x/TiO_2$  catalysts. It seems important to find out which kind of bonds is most active in the decomposition of chloroaromatics. Both the V=O and V-O-support groups are present in isolated, dimeric and polymeric species, while V-O-V groups only appear in dimeric and polymeric species. Most studies suggest that the most active phases are the V-O-V groups present in dimeric and polymeric species or else small V<sub>2</sub>O<sub>5</sub> crystals.

Muhler and co-workers [228] prepared V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> exposing only isolated vanadyl species by washing these catalysts with aqueous solutions of ammonia and comparing their activity with those same samples without ammonia treatment. In toluene decomposition, the monomeric vanadyl species were related to oxidative adsorption, while polymeric vanadia species were essential for  $O_2$  dissociative chemisorption and also favored faster oxygen replenishment. Even though the reactant is toluene, it is still instructive to understand the role of vanadyl species. Graham et al. [101] found for chlorobenzene decomposition that highly V-loaded V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts performed better in the presence of crystalline  $V_2O_5$ , indicating the importance of the presence of V<sub>2</sub>O<sub>5</sub> crystallites. Schimmoeller et al. [229] suggested that the most active species are the V-O-V bonds, keeping sufficient interaction with the support, either being directly connected to the support or close to a V-O-Ti bond. This could explain the existence of a maximum of activity for intermediate loading of vanadium with dominantly polymeric and small crystalline  $VO_x$  species [227]. Debecker et al. [230] used time-of-flight secondary ion-mass spectroscopy to show that catalysts exhibiting a higher proportion of V-O-V bonds were relatively more active than catalysts with similar loading, yet exhibiting a lower condensation degree for surface vanadia species.

However, Krishnamoorthy et al. [58,59,167] showed that the turnover frequency

(TOF) of V-based catalysts is independent from the vanadia loading, suggesting that V-O-V bonds fail to participate in the oxidation of chloroaromatics, whereas the oxygen in the V-O-support is probably involved in the oxidation process, since catalytic activity is strongly influenced by the support composition [69].

#### 4.2.1.2. The role of acid sites

Acid sites play a crucial role in catalytic oxidation, since they are strongly related to the adsorption step of chloroaromatics. The specific roles of Lewis and Brønsted sites, however, are still strongly debated. Bertinchamps et al. [68] suggest that Lewis sites, as represented mainly on the TiO<sub>2</sub> support, are associated with the dispersion of the active phase (VO<sub>x</sub>) or of those promoters (WO<sub>x</sub> or MoO<sub>x</sub>) typically used in these formulations. Brønsted acid sites are available mainly on the supported active phases and their promoters: they are the sites on which chloroaromatics adsorb. According to Larrubia and Busca [79], Lewis sites are involved in the first adsorption step of the oxidation of dichlorobenzene, through which the chlorine atom adsorbs weakly on Lewis sites, while dibenzofuran adsorbs through the oxygen atom of its furan ring. Also Albonetti et al. [148] concluded that both Lewis sites and Brønsted acid sites act as adsorbing sites and that chloroaromatics adsorb via chlorine abstraction on the Lewis sites and via hydrogen abstraction on Brønsted acid sites. Both pathways are illustrated in Figure 6. However, the presence of numerous Brønsted acid sites leads to incomplete decomposition of chlorobenzenes [146, 148].



Figure 6. Reaction mechanism for oxidizing o-dichlorobenzene on vanadium supported catalysts in presence of [A] a high number of Brønsted acid sites; [B] prevailing Lewis acid sites. [148]

Some strategies for improving the catalyst activity precisely aim at promoting adsorption by increasing the number, strength, or density of surface acid sites, e.g. by using MoO<sub>3</sub> or WO<sub>3</sub> promoters for V<sub>2</sub>O<sub>5</sub>. Semi-volatile compounds like PCDDs and PCDFs have such high boiling points that adsorption is easy and no longer rate-limiting. Consistently, the activation energy for decomposing dioxin is very different from that of chlorobenzenes [158]. Therefore, for boosting dioxin decomposition, catalyst development should be focused on enhancing the oxidation potential and not surface acidity [174].

#### 4.2.2. MnO<sub>x</sub>-based Catalysts

 $MnO_x$ -based catalysts show clear activity for removing chloroaromatics, but they also suffer from chlorine poisoning. Therefore, compared with VO<sub>x</sub>-based catalysts, less attention is paid to this group. As far as their loading is concerned, a trend similar to those of VO<sub>x</sub>-based catalysts is observed: for rising Mn load the conversion of

chloroaromatics first strongly surges and then eventually drops, after a certain threshold is reached [107, 109, 149, 231].

For supported  $MnO_x$  catalysts, highly dispersed  $MnO_x$  species at low loading are favored, while at high Mn loads less active  $Mn_2O_3$  and  $MnO_2$  are inevitably formed. Although the specific values of turning points vary a lot in different papers - perhaps due to different preparation methods - the conversion trends of chloroaromatics versus loading are consistent internally. Li and colleagues [231] studied the catalytic performance for removing chlorobenzenes by  $MnO_x$ , supported on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and  $SiO_2$ ; MnO<sub>x</sub>/TiO<sub>2</sub> yields the highest activity, due to the better dispersion of manganese oxides. Although  $MnO_x$  can be extensively dispersed on  $Al_2O_3$ , their strong interaction  $(Mn^{3+}O-Al^{3+})$  deters their reducibility. There are significant differences between H<sub>2</sub>-TPR results for fresh and used catalysts, signifying that the oxidation state of Mn species changed during the catalytic oxidation process: highly dispersed  $MnO_x$  species converted into  $MnO_xCl_y$ , the active phase of the later process phases (after about 10 hours) yet exhibiting lower activity than highly dispersed MnO<sub>x</sub>. Yang et al.[109] investigated the catalytic performance of MnO<sub>x</sub>/TiO<sub>2</sub>, prepared with distinct Mn/Ti atomic ratios, using sol-gel, solvothermal, and coprecipitation methods. Among these, the catalyst with an atomic ratio of Mn/Ti =1:4 and prepared by sol-gel methods showed the highest activity between  $100 \sim 300$  °C. The presence of a small amount of rutile-TiO<sub>2</sub> in  $MnO_x/TiO_2$  prepared by sol-gel may be beneficial to attain this high activity.

The performance of bulk phase  $MnO_x$  has also been studied and its reactivity is closely associated with the catalyst morphology [232-235]: the exposed crystal facets exert an important effect on the reactivity of the catalysts [236-239]. Figure 7 shows SEM images of  $MnO_x$  in its various shapes: rods, wires, tubes and even flower-like
ones. Yang et al. [234] investigated four types of of octahedral MnO<sub>2</sub> molecule sieves  $(\alpha, \beta, \gamma, \alpha, \beta)$  on catalytic performance tested on hexachlorobenzene at trace concentration. Apparent differences in morphology, adsorption ability and redox properties were observed. The catalytic activity of these octahedral molecular sieves decreases in the sequence:  $\delta > \alpha > \gamma > \beta$ -MnO<sub>2</sub> and the presence of surface Mn<sup>2+</sup> is beneficial to the mobility of oxygen species. A high removal efficiency was also obtained when using  $\delta$ -MnO<sub>2</sub> for decomposing a mixture of gaseous pentachlorobenzene, hexachlorobenzene, and polychlorinated biphenyls.



Figure 7. SEM images of (a, b) rod-like MnO<sub>2</sub>, (c, d) wire-like MnO<sub>2</sub>, (e, f) tube-like MnO<sub>2</sub>, and (g, h) flower-like Mn<sub>2</sub>O<sub>3</sub>. [240] Copyright 2012 ACS Publications.

Deactivation of supported MnO<sub>x</sub> catalyst was observed during the catalytic oxidation of chloroaromatics and ascribed to the formation of chlorinated and oxychlorinated manganese species. These are less active and cover more active phases, resulting in reduced catalytic activity [70, 107, 231]. Species of ClMnO<sup>-</sup>, Cl<sub>2</sub>MnO<sup>-</sup>, Cl<sub>3</sub>Mn<sup>-</sup> were detected and these chlorinated species were more prominent with rising Mn load, indicating that chlorine interacted more markedly with catalysts containing higher

proportions of crystalline  $MnO_x$  [70].

#### 4.2.3. CeO<sub>x</sub>-based Catalyst

 $CeO_2$  has a high oxygen storage capacity, linked to the presence of abundant oxygen vacancies and both the surface and bulk oxygen of can directly participate in reactions thereby stimulating the creation of oxygen vacancies. The energy required to form an oxygen vacancy (= its reducibility) is relatively low, and this makes ceria an interesting candidate for producing catalysts destined for Mars-van Krevelen-type reactions. Upon creating an oxygen vacancy (bulk as well as surface), the electrons left behind localize in ions, reducing these from Ce<sup>4+</sup> to Ce<sup>3+</sup>. Density functional theory (DFT) predicted and scanning tunneling microscopy (STM) confirmed the presence of multiple configurations of Ce<sup>3+</sup>-ions, providing evidence for their presence in different coordination environments [243]. DFT and Perdew-Burke-Ernzerhof generalized gradient approximation (PBE) calculations confirmed that the  $O_2$  adsorption into a surface vacancy results in an electron transfer from  $Ce^{3+}$  to  $O_2$ , yielding superoxo,  $O_2^{--}$  and peroxo,  $O_2^{2-}$  surface species [98, 241]. Ceria surfaces will undergo vacancy replenishment even without metal doping, indicating that the limiting step in the activation of  $CeO_2$  is the creation of oxygen vacancies. Recent literatures demonstrated that the doping of transition metal, noble metal, or rare earth metal to ceria oxides can lower oxygen vacancy formation energies. Table 2 lists the formation energy of an oxygen vacancy for several doped cerium oxides. Moreover, DFT calculations of the length of cation-oxygen bonds confirmed that doping ceria with transition metal (Mn, Fe, Co, Ni, and Cu) or noble metal (Pd, Pt, and Ru) induced longer cation-oxygen bonds for both dopant and cerium ions (Figure 8), which generally represents easer oxygen release from dopant and ceria oxides [242].



Figure 8. (a) Distribution of M-O bond lengths of CeO<sub>2</sub>, RuO<sub>2</sub> and Ce<sub>28</sub>Ru<sub>4</sub>O<sub>62</sub> (M = Ru, Ce); (b) Distribution of M-O bond lengths of CeO<sub>2</sub>, MnO<sub>2</sub>, PdO, Ce<sub>28</sub>Mn<sub>4</sub>O<sub>62</sub> and Ce<sub>27</sub>Mn<sub>4</sub>Pd<sub>1</sub>O<sub>61</sub> (M= Ce, Mn and Pd). [242] Copyright 2010 ACS Publications.

Table 2. Defect Formation Energies,  $\Delta E_d(\frac{1}{2} O_2)$ , of non-doped and doped CeO<sub>2</sub>, in eV. [243] Copyright 2013 ACS Publications.

surface			$\Delta E_d(1/2O_2)$	
(111)	CeO <sub>2</sub>	PBE+U(5)	2.87	
	$Zr_{0.25}Ce_{0.75}O_2$		2.35	
	$La_x Ce_{1-x}O_2$	PW91+U(5)	0.90	
	CeO <sub>2</sub>	rPBE	3.01	
	Au <sub>0.06</sub> Ce <sub>0.94</sub> O <sub>2</sub>		-0.36	
			1.46 <sup>a</sup>	
	CeO <sub>2</sub>	PBE+U(4.5)	2.15	
CIP -	$Au_xCe_{1-x}O_2$		0.32	
	)		1.61 <sup>b</sup>	
	$Cu_{0.08}Ce_{0.92}O_2$	PBE+U(5)	0.04	
			2.17	
	CeO <sub>2</sub>	PBE+U(6.3)	2.08	
6	$Ru_{0.125}Ce_{0.875}O_2$	PBE+U(6.3)	0.87	
	Fe <sub>0.125</sub> Ce <sub>0.875</sub> O <sub>2</sub>	PBE+U(5)	0.68	
(110)	CeO <sub>2</sub>	PBE+U(5)	2.30	
	$Zr_{0.25}Ce_{0.75}O_2$		0.94	
	CeO <sub>2</sub>	PBE+U(5)	1.99	
	$Ti_{0.04}Ce_{0.96}O_2$		0.31	
	$Zr_{0.04}Ce_{0.96}O_2$		0.48	
	$Hf_{0.04}Ce_{0.96}O_{2}$		0.36	

$La_x Ce_{1-x}O_2$	PW91+U(5)	0.64
CeO <sub>2</sub>	PBE+U(5)	2.07
$Au_xCe_{1-x}O_2$		-0.08

<sup>a</sup>Second vacancy. <sup>b</sup>Creation of a second vacancy

However, when decomposing chloroaromatics, the deactivation of CeO<sub>2</sub> is very fast, owing to the too strong interaction of CeO<sub>2</sub> and chlorine species at temperatures <  $400 \,^{\circ}$ C. The stability of CeO<sub>2</sub> could be improved significantly if the chlorine species adsorbed on these CeO<sub>2</sub> surfaces were removed more rapidly. The removal rate of Cl from the catalytic surface depends on additives as well as on temperature according to studies on the decomposition of chloroaromatics over Mn-[115-120], Ru- [96, 121-123] and other transition metal doped CeO<sub>x</sub>-catalysts. Normally, chlorine is removed faster at higher temperature following the oxidation of HCl to Cl<sub>2</sub> which desorbs from the catalyst surface more easily. So, there is a certain temperature threshold above which ceria-catalysts show stable performance during the catalytic oxidation of chloroaromatics. The promoting effects of additives, including Mn, Ru, Mg, Cr, Cu, etc., are discussed in Section 5.2.2.

The formation of chlorinated by-product (e.g. dichlorobenzene) was detected during the catalytic decomposition of chlorobenzene over Ru-CeO<sub>2</sub> [96]. Lewis acids, such as FeCl<sub>3</sub>, AlCl<sub>3</sub>, SbCl<sub>3</sub>, and MnCl<sub>2</sub>, are industrially applied as catalysts for the production of chlorobenzene and dichlorobenzene; the generation of higher chlorinated benzenes can be attributed to the partial chlorination of RuO<sub>2</sub> to Ru (oxy-)chlorides acting as catalyst for these chlorination reactions [96].

#### 4.2.4. Fe-based catalysts

Due to their low price and negligible toxicity, supported  $FeO_x$  catalysts were recently proposed for decomposing chloroaromatics. Their activity for chlorine mineralization

is outstanding, as  $Cl_2$  is the only Cl-product detected [131]. Both hydro-dechlorination and oxidation reactions occur over such FeO<sub>x</sub>-based catalysts. Still, these show poor activity for converting chloroaromatics below 350 °C even 400 °C [81, 87]. The addition of calcium, as CaCO<sub>3</sub> or CaO, significantly improves not only catalytic activity, but also its resistance to water vapor (see section 5.2.1). Khaleel and Al-Nayli [131] compared the catalytic performance of iron and titanium mixed oxides, i.e. Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and Fe<sub>x</sub>Ti<sub>y</sub>O, prepared by respectively wetness impregnation and sol-gel methods. The Fe<sub>x</sub>Ti<sub>y</sub>O-catalyst revealed excellent activity and stability for converting chlorobenzene and attained complete conversion already at 325 °C. According to Ma et al. [153] the Fe/Ti-ratio significantly influences upon the crystal phase ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> vs.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and crystal size of Fe<sub>2</sub>O<sub>3</sub> and these strongly correlated with the activity of Fe<sub>x</sub>Ti<sub>y</sub>O catalyst. Practically, the Fe<sub>18</sub>Ti<sub>2</sub>O<sub>x</sub> catalyst with the largest concentration and the smallest crystals of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> exhibits highest reactivity for 1,2-dichlorobenzene decomposition.

**4.3.** Perovskite-type catalysts

Perovskite-type catalysts feature a general formula ABO<sub>3</sub>, where A is typically a rare earth or earth alkali ion and B a 3d, 4d or 5d transition metal ion. Substitution of both A and B sites varies the composition and symmetry of the mineral and can create cation or anion vacancies, both influencing greatly upon reactivity [157, 244]. Few ABO<sub>3</sub>-type perovskites (A = La, Y, Gd or Nd; B = Cr, Co, Fe or Mn) were reported for decomposing chloroaromatics, due to the high operating temperature required, usually > 500 °C [139, 157, 245]. When put on stream, moreover, most perovskite-catalysts undergo an initial deactivation period, related to a reduction of specific surface area. For example, with a feed of 1,2-dichlorobenzene at 500 °C, LaCoO<sub>3</sub> showed severe deactivation during 5 hours, due to the breaking down of the

original structure to LaOCl and  $Co_3O_4$  [157]. Afterwards, activity remains stable. The substitution of La in the A-site with other rare earth cations could result in stabilizing the catalytic surface area and prevent the formation of LaOCl and concomitant loss in surface area [157]. Lu et al. [245] studied the partial replacement with Sr of La in LaMnO<sub>3</sub>; among the resulting structures, La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> presented the highest activity as well as large oxygen mobility, ascribed to the rapid removal of chlorine species from the catalyst surface.

#### 4.4. Conclusions

Although  $MnO_{x^-}$ , FeO<sub>x</sub>-, and CeO<sub>x</sub>-based composite oxide catalysts show fair reactivity relative to the catalytic decomposition of chloroaromatics, their application is severely restricted by chlorine poisoning. Numerous studies were conducted to improve their resistance to Cl poisoning, but the progress realized is still inadequate. In contrast, vanadium oxides exhibit both relatively high and stable catalytic activity. Similar vanadia species (V=O, V–O–V, and V–O–support) generally appear on all catalytic surfaces, independently of the nature of the support used. Among these the most active vanadia species seem to be the V-O-V groups existing in dimeric and polymeric species or else as small V<sub>2</sub>O<sub>5</sub> crystals.

#### 5. Improving catalysts

Much research is devoted to improving or refining certain critical catalytic characteristics. Such changes and adaptations address several features, such as the tuning of the support, the addition of promoters/dopants, the adaptation of preparation methods, etc. These techniques are applied to increase the number of active sites and intrinsic activity of the catalyst and thereby, to improve its catalytic performance, i.e., activity, selectivity, stability and lifetime.

#### 5.1. Tuning the support

The activity and stability of catalysts are determined not only by their active phases, but also by their carrier and its interactions with those active phases. Catalyst carriers can provide suitable surface properties, facilitate the dispersion of active phases on their surface, and prevent or retard the aggregation of active phases at high temperature. The dispersion of one oxide on another possibly proceeds by (1) surface diffusion, driven by concentration gradients, (2) gas-phase transport and deposition or adsorption onto the support surface, or (3) solid-solid wetting, driven by free energy gradients. Both Haber et al. [246, 247] and Knozinger et al. [248] proposed that (3) is the chief factor of influence when dispersing active phases over the support. The catalyst carrier conceivably can be altered to improve the dispersion of active phase on its surfaces with high surface area and suitable porosity. The three methods used for tuning the catalyst carrier are surface modification, structure optimization and turning to composite carriers.

The classical approach towards surface modification is its acid treatment to create additional hydrophilic functions at the surface. Compared with traditional TiO<sub>2</sub>, for example, sulfated TiO<sub>2</sub> (containing certain amount of sulfates) comprises strong and abundant Lewis acid sites, promoting the dispersion of active phase VO<sub>x</sub> and promoters MoO<sub>x</sub> or WO<sub>x</sub> over the catalytic surface [249]. This step produces a markedly enhanced activity, accelerating the decomposition of PCDD/Fs [174]. Also, the crystallinity and texture play an important role regarding the catalyst's structure and thus can both be optimized, e.g.:

V<sub>2</sub>O<sub>5</sub> impregnates anatase-TiO<sub>2</sub> surfaces, rather than rutile-TiO<sub>2</sub> preferentially
 [250]. Therefore, TiO<sub>2</sub> with higher anatase content facilitates the dispersion of VO<sub>x</sub> [214].

- Nano-TiO<sub>2</sub> (Degussa P25 [251]) secures a higher specific surface area than conventional TiO<sub>2</sub>. This support thus stimulates the dispersion of VO<sub>x</sub>, as well as the interactions between V and its carrier, boosting catalytic activity thereby [252].
- Chin et al. [145] prepared TiO<sub>2</sub> with high specific surface area by chemical vapor condensation. Surprisingly, this area enlarged after deposition of V<sub>2</sub>O<sub>5</sub>, merely by adjusting the heating and synthesis temperature.
- A CrOOH aerogel with high surface area (> 600 m²/g) was applied as support of Pt for decomposing chlorobenzene [253]. Full conversion was achieved, with a selectivity to CO<sub>2</sub> of >95%. More importantly, after 200 h no deactivation was observed, probably benefiting from a highly efficient redox cycle [254]: Cr<sup>III</sup>
  []OH ↔ Cr<sup>IV</sup> [O]O, where [] represents an oxygen vacancy

Compared with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the main disadvantages of anatase TiO<sub>2</sub> are high cost, relative low surface area, and low thermal stability. Composite carriers may improve the catalytic properties by combining advantages of each individual support separately. A TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite carrier [91, 94, 107, 231] was prepared profiting from the high specific surface area supplied by Al<sub>2</sub>O<sub>3</sub>. On this alumina carrier TiO<sub>2</sub> disperses as a monolayer where the active phases scattered. Accordingly, the reducibility of catalysts augmented significantly. Similarly, TiO<sub>2</sub>-SiO<sub>2</sub> composite carrier [146] was applied to inhibit the aggregation of active phases thus slow down the deactivation of the catalysts. The addition of Si also inhibits sintering of anatase TiO<sub>2</sub> and preserves the initial surface area of the catalysts [225].

The graphene surface of carbon nanotubes (CNTs) is easily polarized and thus likely to act as an electron donor, when coming in contact with strong electron acceptors such as aromatic rings, occurring in chlorobenzenes [255], nitrobenzenes [255], and

PCDD/Fs [256-258]. The  $\pi$ - $\pi$  interaction between benzene ring and CNTs explains the excellent adsorption of aromatic compounds on CNTs. Compared with AC, CNTs present stronger adsorption affinity and capability [256, 257] and show higher removal efficiency and durability [258]. Moreover, both the number of its acidic surface sites and the adsorption capacity significantly surge after acid pre-treatment [255]. Based on the outstanding adsorption of PCDD/Fs and also of chlorobenzenes, TiO<sub>2</sub>-CNTs are studied as composite carrier for transition metal oxides and display excellent catalytic activity for the oxidation of chloroaromatics, especially at low temperature. The activity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (prepared hydrothermally), MnO<sub>x</sub>/TiO<sub>2</sub>, and CuO<sub>x</sub>/TiO<sub>2</sub> catalyst was superior to expectations and accompanied by higher CO<sub>2</sub> selectivity after adding CNTs [90, 105, 108].

Figure 9 shows the homogeneous deposition of active particles on the outer surface of CNTs with a diameter lower than 10 nm. In brief, CNTs addition allows several improvements: a better dispersion of the active phases [105, 108], stronger adsorption affinity and capability [256, 257], and promoting  $\pi$ - $\pi$  interaction between benzene rings and CNTs [255-257]. However, CNTs are also prone to aggregate, due to the strong van der Waals forces, forming bundles or loose, tangled agglomerates [259]. The expected aggregation of CNTs was already reported for CNT-containing catalysts [105] and indeed reduces surface area [260].



Figure 9. SEM and TEM images of  $V_2O_5/TiO_2$ -CNT composites: (a)  $V_2O_5/TiO_2$ , (b)  $V_2O_5/TiO_2$ -(0.8wt.%)CNTs (c)  $V_2O_5/TiO_2$ -(5.1wt.%)CNTs, (d)  $V_2O_5/TiO_2$ -(6.2wt.%)CNTs, (e)  $V_2O_5/TiO_2$ -(8.6wt.%)CNTs, (f)  $V_2O_5/TiO_2$ -(8.6wt.%)CNTs after 150 h activity test, and (g) TEM image of  $V_2O_5/TiO_2$ -(8.6wt.%)CNTs. [105] Copyright 2011 ACS Publications.

### 5.2. Promoters and dopes

Catalytic properties such as ion valence, acidity, surface structure, crystal size,

adsorption capacity, reducibility, etc., can all be adjusted by adding suitable

promoters or dopants, possibly with improved activity, selectivity and/or stability.

The fundamentals are discussed in Section 5.2.1.

Ceria is renowned for its storage capacity for oxygen, yet it can be highly enriched

with suitable dopes. These Ce-based catalysts are discussed in 5.2.2.

#### 5.2.1. VO<sub>x</sub>-, MnO<sub>x</sub>-, and FeO<sub>x</sub>- based catalysts

Both V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub> are efficient commercial catalysts, allowing a total oxidation of a variety of pollutants [86, 261, 262]. Initially invented for the selective catalytic reduction of NO<sub>x</sub> by ammonia or other reducing agents [263], they also proved effective enhancing the catalytic decomposition of chloroaromatics and dioxins. The addition of WO<sub>3</sub> or MoO<sub>3</sub> improves the catalytic activity and the stability of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, by suppressing sintering and retarding the phase transformation from anatase to rutile-TiO<sub>2</sub> [264]. This widens the effective temperature range [216] and increases the Brønsted acidity of the catalyst [86], since both WO<sub>3</sub> and MoO<sub>3</sub> hold these acid sites at their surface [249]. Besides, simultaneous addition of MoO<sub>x</sub> (WO<sub>x</sub>) and VO<sub>x</sub> with a molar ratio Mo/V (W/V) equal to 1 leads to superior catalytic activity [249]. Other secondary phases (i.e., CrO<sub>x</sub>, MnO<sub>x</sub>, CeO<sub>x</sub>, SnO<sub>x</sub>, NbO<sub>x</sub>) addition to VO<sub>x</sub>/TiO<sub>2</sub> results unsatisfactory performances, suffering from either poor activity or low resistance to chlorine poisoning [68, 181, 265].

Doping with Ag introduces electrophilic oxygen and induces a higher oxidation state of vanadium in  $V_2O_5/TiO_2$ , improving catalytic performance under certain conditions, without chlorination of Ag [266, 267]. Also, the order of impregnation of vanadium on TiO<sub>2</sub> is important in shaping its catalytic performance, probably related to the dispersion of vanadium on the carrier and the access of gaseous oxygen to Ag [268]. Yang et al. [164] introduced Cu into the framework of octahedral manganese oxide molecular sieve (OMS) and obtained greatly improved performances, both in activity and stability. In the presence of an appropriate amount of Cu<sup>2+</sup>, the resulting Cu-doped manganese oxide octahedral molecular sieve assumes a layer structure, with amplified specific surface area and pore volume (Figure 10). Moreover,

Cu-OMS becomes better reducible, due to the formation of Cu-O-Mn structures in which the lattice oxygen is activated via electronic delocalization effects [269]. In addition, doping with Cu can significantly improve the stability of the catalyst, due to an accelerated removal of surface Cl via the Deacon reaction, catalyzed by CuO. Also, Cu addition to MnO<sub>x</sub> can form  $Mn_{3-x}Cu_xO_4$  (x = 1.4 to 1.5) incomplete spinel phases with better redox properties [270-272]. The presence of such spinel phases is responsible for the superior reactivity of the catalysts during the catalytic decomposition of chlorobenzene [273].



Figure 10. FESEM images of (a) pristine OMS, (b) Cu(0.2)-OMS, (c) Cu(0.4)-OMS, and (d) Cu(0.6)-OMS. The catalysts denoted as Cu(0.2)-, Cu(0.4)-, and Cu(0.6)- with the number referring to the Cu/Mn molar ratio in the precursor solution of 0.2, 0.4, and 0.6, respectively. [164]

Doping Fe<sub>2</sub>O<sub>3</sub> with Ca leads to smaller pore sizes, higher specific surface areas and smaller crystal sizes, all advantaging catalytic activity [81, 87, 154]. Further, CaCO<sub>3</sub> or CaO serve as a potential sink for chlorine ions: FeCl<sub>3</sub> is produced by reaction of FeO<sub>x</sub> with chloroaromatics, yet, as it exchanges Cl<sup>-</sup> for O<sup>2-</sup> on CaCO<sub>3</sub> or CaO, the active phase, FeO<sub>x</sub> is regenerated:

$$FeCl_3 + CaO \rightarrow FeO_x + CaCl_2$$

Also, an appropriate amount of Ca induces a phase transition from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, resulting in higher surface chemisorbed oxygen and low-temperature reducibility, responsible for better performance [87].

#### 5.2.2. CeO<sub>x</sub>-based catalysts

Numerous catalysts have been based on  $\text{CeO}_x$ .  $\text{CeO}_x$ , however, is easily deactivated, due to its strong interactions with chlorine species, as already mentioned in section 4.2.3. For this class of catalysts, promoters are proposed trying to remove Cl from the catalytic surface faster and prevent deactivation.

#### 5.2.2.1. Mn doped CeO<sub>x</sub>-based catalyst

Manganese effectively removes chlorine species from CeO<sub>2</sub> active sites by forming manganese (oxy-) chlorides, which are quickly oxidized by gaseous oxygen, recovering MnO<sub>x</sub> species [274]. Thus, MnO<sub>x</sub> is a widely applied dopant of those CeO<sub>2</sub> catalysts used for decomposing chlorinated hydrocarbons (CHCs). Studies show that the chlorobenzene conversion rises with Mn content, since the reducibility of manganese species is enhanced by a high degree of coordinative unsaturation [115, 117, 118]. Additionally, the resulting Mn<sub>x</sub>Ce<sub>y</sub>O catalysts have more chemisorbed oxygen surface species, assisting in removing any chlorine produced during catalytic reactions and they exhibit to some extent a better stability, combined with a high

selectivity to  $CO_2$ , up to 99.5% [115].

Also Mg was added to such a  $Mn_xCe_yO/Al_2O_3$  catalyst, considering its positive effect on the formation of smaller sized active phases on the support [117]. The introduction of Mg may decrease the interaction of both manganese and cerium oxides with  $Al_2O_3$ and promote their dispersion on the carrier. The available XPS results suggest that the interaction of CeO<sub>2</sub> with  $Al_2O_3$  inhibits to some extent the formation of  $Mn_xCe_yO$ solid solution, whereas the introduction of Mg restrains this interaction. At high temperature, however, the structure of  $Mn_xCe_yO$  solid solutions is no longer stable and both CeO<sub>2</sub> and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> are likely to separate from this solid solution. To improve its stability at higher temperatures, La, Mg and Sn are added [117, 119, 275]. In the case of Sn-MnCeLaO<sub>x</sub>, doping with Sn can also significantly increase the amount of surface chemisorbed oxygen, accelerating the removal of chlorine from catalytic surfaces by the Deacon Reaction and impeding the formation of less effective MnO<sub>x</sub>Cl<sub>y</sub> species.

### 5.2.2.2. Ru doped CeO<sub>x</sub>-based catalyst

Due to their high activity, stability and easier  $Cl_2$  evolution, Ru-based catalysts have been industrially applied for producing  $Cl_2$  via the Deacon Reaction. Therefore, the introduction of Ru is expected to improve the stability of a CeO<sub>2</sub>-based catalyst, by rapidly removing various Cl species from active sites in the form of  $Cl_2$  gas. Compared with CeO<sub>2</sub>, a Ru-CeO<sub>2</sub> catalyst showed indeed better activity and stability at temperatures above 275 °C [96, 121]. However, at low temperature (< 200 °C) Ru-CeO<sub>2</sub> revealed poor activity and this catalytic activity declined further with rising Ru content. While introducing Ru, the concentration of oxygen vacancies of CeO<sub>2</sub> dwindled [121]. Surprisingly, in later papers from the same group [123], Raman spectroscopy indicated that the number of oxygen vacancies augmented with the

insertion of Ru. So, the reason why Ru-CeO<sub>2</sub> exhibited lower activity at low temperature is still unclear.

RuO<sub>2</sub> supported on TiO<sub>2</sub> displays high activity and good stability in the Deacon reaction [276-278]; hence, the effect of TiO<sub>2</sub> doping Ru-CeO<sub>2</sub> catalysts was investigated during chlorobenzene decomposition [122]. The activity of Ru/Ti-CeO<sub>2</sub> catalysts is significantly influenced by the amount of Ti introduced [122]. Even at low temperature (200 °C) outstanding reactivity was observed over Ru/Ti(5% wt.)-CeO<sub>2</sub>. The higher activity of Ru/Ti–CeO<sub>2</sub> was ascribed to the higher density of exposed CeO<sub>2</sub> (110) and (100) lattice facets and oxygen vacancies [279]. Additionally, the resulting morphology of CeO<sub>2</sub> (e.g., nano-rods, -cubes and -octahedra) greatly affects the quality of the interactions between the Ru-species introduced and the CeO<sub>2</sub> carrier [123]. Most favorable for Ru activation are CeO<sub>2</sub> nanorods, leading to more Ru–O–Ce bonds and Ru<sup>4+</sup> and greater mobility of oxygen species, all resulting in a lower activation energies for chlorobenzene decomposition. Moreover, the lowest amount of dichlorobenzene by-products was detected over CeO<sub>2</sub> nanorods supported Ru catalyst.

#### 5.2.2.3. Other doped CeO<sub>x</sub>-based catalysts

Doping with other transition metals (e.g. Co, Cu, Fe, Zr, V, Cr, and Ni) resulted in improved reactivity in chloroaromatic conversion [126]. In H<sub>2</sub>-TPR profiles, the reduction temperatures shift towards lower values after doping with transition metals. Some of these are incorporated into the fluorite lattice of ceria, leading to a higher density of oxygen vacancies, resulting in higher redox-ability of the doped catalysts. Among these, the Cu-Ce-O<sub>x</sub> catalyst shows an outstanding activity for chlorobenzene decomposition, attributed to its large specific area and abundant interfaces. In the presence of a small amount of manganese more Cu and Mn-ions can be introduced

into the ceria lattice [226]. Manganese species, however, negatively influence copper dispersion at relative high copper loadings, i.e. a molar ratio of Cu/(Cu+Mn+Ce) = 0.2. The interaction among Cu, Mn, and Ce shows synergistic effects, improving the reducibility of the mixed metal oxides. A Cu<sub>0.15</sub>Mn<sub>0.15</sub>Ce<sub>0.7</sub>O<sub>x</sub> catalyst exhibits the best performance in chlorobenzene oxidation, attaining a 95% chlorobenzene removal and a selectivity for CO<sub>2</sub> of up to 99.5% at 264°C.

#### **5.3. Preparation methods**

The most widely used methods for preparing supported noble metal and metal oxide catalysts are impregnation, sol-gel, and co-precipitation. The catalyst preparation method may be modified and adapted to improve the resulting physico-chemical properties (e.g. specific surface area, pore structure, and oxidation state of active phases) and attain a better dispersion of the active phases of the catalyst.

#### 5.3.1. Better dispersion

When using NH<sub>4</sub>VO<sub>3</sub> as solute during the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-preparation by impregnation the predominant vanadium species in the solution depends on the pH-value [280, 281]: VO<sub>2</sub><sup>+</sup> at pH = 1, deca-vanadates at pH = 4 or 5.5 and VO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> at pH = 5.5. Therefore, an effect of pH-value on the impregnation of VO<sub>x</sub> on TiO<sub>2</sub> can be expected. Chiker et al. [281] reported that the best dispersion of vanadyl as active phases is obtained by deposition of VO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> at pH=5.5. According to Gao et al. [282], increasing the pH value of the gel mixtures during the preparation augmented the isolated and polymeric vanadium species incorporated in SBA-15 (mesoporous molecular sieves), while the crystalline VO<sub>x</sub> species diminished. The surface areas are doubled after vanadium impregnation by chemical vapor deposition, resulting in better dispersion, a higher oxidation state of vanadium, and thus better performance on 1,2-dichlorobenzene decomposition [145].

In order to increase the amount of  $VO_x$  available at the outer surface of TiO<sub>2</sub>, Choi and Suh [227] hydrolyzed titanium tetrabutoxide Ti(OBu)<sub>4</sub> (Bu = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), before adding vanadium isopropoxide and thus promoted catalytic activity:  $VO_x$  is located not only at the surface of TiO<sub>2</sub> but also within the TiO<sub>2</sub> structure; the latter is obviously unfavorable.

#### 5.3.2. Structural optimization

An ethylene-glycol-mediated process successfully synthesized three-dimensionally (3D) structured micro/nano materials having hierarchical porous structures, and a particle size at the micron scale [160, 161, 283-285]. Their specific surface area is relatively large and the hierarchical structure effectively inhibits aggregation. In addition, multi-scaled porosity is expected to reduce the resistance to diffusion, favoring adsorption/desorption. Optimizing these structural properties contributes to the decomposition of chloroaromatics [160, 161].



Figure 11. SEM images of (a)  $Fe_2O_3$ , (b) FeCa5, (c) FeCa10 and (d) FeCa20 catalysts. In FeCa5, FeCa10, and FeCa20 the number refers to the nominal content of Ca, i.e. 5, 10, and 20 mol %, respectively.[87]

Structure directing agents play an important role in surface modification and controlled structure and morphology of synthetic catalysts and thus are often used to obtain catalysts with good texture properties [81, 87, 144, 153, 154]. Pluronic P123 with a composition (ethylene oxide)<sub>20</sub> – (propylene oxide)<sub>70</sub> – (ethylene oxide)<sub>20</sub> was used by Jung et al. [144] in the preparation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>. They optimized catalysts with high specific area and good porosity by adjusting the P123/Ti ratio (a ratio of 0.05 showed the best results). The introduction of cetyltrimethylammonium bromide (CTAB) induces a large number of interstices among catalyst particles [154]. Ma et al. [153] obtained Fe<sub>18</sub>Ti<sub>2</sub>O<sub>x</sub> with a worm-like mesoporous structure by using an

appropriate dosage (9 nmol) of CTAB, which exhibited the highest activity. The same group successfully synthesized Ca-doped FeO<sub>x</sub> hollow microspheres by using carbon microspheres as hard template. Pure Fe<sub>2</sub>O<sub>3</sub> hollow microspheres constitute of small nanoparticle with interconnected textural mesopores (Figure 11) and attained at 350 °C a 1, 2-dichlorobenzene conversion efficiency almost 50% higher than that of commercial Fe<sub>2</sub>O<sub>3</sub> [87].

#### **5.4.** Conclusions

This section surveys some suitable methods for refining certain critical catalytic characteristics and addressing the catalytic support, the addition of promoters and dopants, the preparation methods chosen, etc. These techniques are quite diverse, yet they all aim at improving catalytic performance, i.e., activity, selectivity, stability and useful lifetime.

Catalyst carriers provide suitable surface properties to facilitate the dispersion of active elements over their surface and prevent or retard the aggregation of active phases at high temperature. Tuning the catalyst carrier may proceed by surface modification, structure optimization and the use of composite supports, such as those incorporating carbon nanotubes. A classical surface adjustment is acid treatment, to create additional hydrophilic functions at the surface.

Generally, the selection of promoters proceeds empirically and their results vary with the nature of the active phases: WO<sub>3</sub>/MoO<sub>3</sub> is frequently used for promoting V<sub>2</sub>O<sub>5</sub>-based catalysts, Cu-promotors for supported MnO<sub>x</sub>, and Ca dopants for FeO<sub>x</sub>-based catalysts. Their promoting effect follows from a better dispersion, stronger acidity, faster mobility of oxygen species (amplified redox properties), sturdier stability, etc.

#### 6. Deactivation and possible regeneration

These catalytic post-combustion systems often operate in a complex, incompletely defined and variable environment and have the potential for generating undesired by-products, particularly after deactivation of the catalyst. Loss of activity may originate from fouling, coking, poisoning, sintering of the catalyst and from volatilization of its active phases. Deactivation reduces the operational capacities of catalytic systems, enhances emissions, and increases operating costs. Moreover, it may occur at times reversibly, not only gradually and progressively, but also suddenly, irreversibly and destructively. Therefore, the study of catalyst deactivation, its forms, mechanism, and possible regeneration is important in evaluating catalyst types and formulations. In addition, the various strategies and means of enhancing catalytic stability and its resistance to poisoning are topical research fields. Fouling or coking comprises the gradual clogging of pores and obstruction of active sites, initiated by the adsorption and deposition of organic substances. These then tend to polymerize and also slowly dehydrogenate, creating coking deposits that steadily amplify and expand over time and progressively convert into coke [286]. Coke

formation may be autocatalytic and also develop from heated or cooled metal or ceramic walls. Some metals or alloy components, such as nickel, notoriously dehydrogenate organics, converting these swiftly into carbon deposits. Such carbon deposits also hinder heat transfer from or to the catalytic compounds.

High temperature conditions considerably enhance the mobility of catalytic elements and thus the sintering tendencies of their structures. A large specific surface area is positive for catalytic activity, yet it may unduly diminish the thermal stability of the catalyst [286]. Temperature excursions (reactor runaway) are a major reason for sintering. The small, most active catalyst sites will be mobilized, rearranged, and

merged into larger aggregates of markedly lower specific surface area. Poisoning of catalysts is due to the strong interaction of active sites with specific reactants, products (including intermediate products) or trace impurities. Sulfur, arsenic, antimony, and chlorine or bromine poisoning [287, 288] all are common in industrial gas effluents.

#### 6.1. Fouling or Coking

Fouling or coking is a gradual covering of active sites by polymers derived from adsorbed organics. This cover reacts steadily by eliminating small molecules, such as water vapor, hydrogen, carbon oxides or the hetero-compounds of sulfur, nitrogen, or halogens. Usually, the contaminated coked catalyst can still be regenerated by oxidative thermal methods (carbon burn-off or gasification), by mechanical methods (vibration, abrasion, washing) or by other physical or chemical methods [289-291]. Carbonaceous deposits fouling catalytic surfaces are commonly called coke. These deposits have an overall chemical composition of  $CH_x$ , where x is typically equal to 0.5 to 0.7 and slowly descends with time. Basically, carbonaceous deposits can be entirely eliminated by gasification with oxygen, water vapor, carbon dioxide, or hydrogen [292]. Oxygen is by far the most reactive of these gases and it may eliminate carbon continuously, as well as periodically. The three other gases are often acting as diluent, to retard coking or fouling, since these reactions often follow second order kinetics. Walker et al. [289] report the relative gasification rates of these different gases are  $O_2$ :  $H_2O$ :  $CO_2$ :  $H_2 = 35,000$ : 1000: 333: 1 (without catalyst). This result provides some guidance for efficient coke removal. Typically, the coke deposited on a catalytic surface is removed after a few hours in a 10 % O<sub>2</sub>/He mixture at 350 °C and the catalyst is then fully regenerated [141].

However, because of the exothermic character of oxidation, catalysts are susceptible to local overheating (hot spots) and subsequent sintering [293]. Thus, steady temperature control is necessary. Moreover, the structure and composition of the deposits have an important impact on gasification. Their rate of gasification can be improved catalytically by, e.g., the presence of Ni [294] or other elements in the residues. A literature search reveals some data on other catalytic elements, potentially active in coke elimination [295].

The regeneration of fouled catalyst thus may proceed in situ, under carefully controlled conditions, comprising temperature + volume of oxygen in the regenerating gas + water vapor and/or carbon dioxide as a diluent. This operation often needs no transfer of the catalyst outside the reactor vessel or tubes. Some industrial operations, such as fluid catalytic cracking of gas-oil, feature an organized transfer of catalyst between a pyrolytic bed and a regenerator bed.

Apart from the necessity of controlling the temperature during regeneration one should also avoid to impair the mechanical stability and integrity of the catalyst during catalyst coking and subsequent regeneration: dilatation could lead to thermal stress; thermal shocks could be accompanied by spalling.

Washing is sometimes possible as a method for catalyst regeneration. The mechanism includes a physical cleaning to dissolve and displace deposited materials and the use of chemical reactions forming soluble salts. For example, macromolecular materials deposited onto the catalyst can possibly be removed by dissolution in solvents such as chlorobenzene or liquid propane [296] and fouling metals can be removed by adding oxalic acid and  $H_2O_2$  to form soluble metal complexes [297]. Additionally, various fouling agents can be removed by physical methods, including shaking and abrasion [298]. Physical methods are typically beneficial when the fouling agents are only

loosely held to the catalyst surface.

#### **6.2.** Thermal deactivation (sintering)

Thermal deactivation refers to the changes in structure and properties of the catalyst caused by its exposure to excessive temperature. Generally, catalyst sintering starts at a temperature of 0.3 to 0.5 times of the melting point, expressed in °Kelvin [299] and it involves the aggregation of active elements reducing surface area, pore volume, and pore size. This aggregation is sparked by the relative thermal stability of finely dispersed vs. bulk chemicals (surface tension) and actually implemented by the thermal movement of atoms or crystals over the surface of their support, so that the sintering of catalysts can be influenced by controlling or retarding the movement of the relevant particles. Thermal deactivation, especially sintering, is essentially irreversible. Hence, to avoid sintering, it is necessary to rise the thermal stability and impede the mobility of active elements in the catalyst or else to develop catalysts that are already active at lower temperatures [300].

Several elements (Pb, Bi, Cl, F, S, etc.) are known to accelerate sintering by facilitating the mobility of some relevant atoms. Other elements (C, O, Ca, Ba, Ce, Ge, etc.) conversely seem to constrain the mobility of metal atoms, inhibiting the agglomeration of active elements [286]. Alumina (Al<sub>2</sub>O<sub>3</sub>) is widely used as support for both transition metal oxide and noble metal catalysts. Burtin et al. [301] studied the influence of adding Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, La<sup>3+</sup>, Zr<sup>3+</sup>, and Th<sup>4+</sup> on the sintering of Al<sub>2</sub>O<sub>3</sub>: adding Mg<sup>2+</sup>, Ga<sup>3+</sup>, and In<sup>3+</sup> facilitates its sintering, whereas Ca<sup>2+</sup>, La<sup>3+</sup>, Zr<sup>3+</sup>, and Th<sup>4+</sup> inhibit it. Beguin et al. [302] noted that Si-containing reactants react with the hydroxyl groups situated at the surface of Al<sub>2</sub>O<sub>3</sub>, forming a layer of solid silica developing on this surface, so that the thermal stability of the catalyst can be improved. Such stability enhances up to ca. 3 wt. % Si, when raising the amount of

deposited Si. Also the addition of BaO, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, or ZrO<sub>2</sub> reduces sintering of  $Al_2O_3$  [301, 303, 304]. The addition of Si also inhibits sintering of anatase TiO<sub>2</sub> and preserves the initial surface area of the catalysts [225].

In addition to sintering high temperatures can cause other alterations, including changes in phase and even in chemical composition (e.g. by the volatilization of active elements). A well-known example is TiO<sub>2</sub> widely used as support: the transformation of anatase to the rutile phase is undesirable and can be suppressed by WO<sub>3</sub> or MoO<sub>3</sub> addition [264, 305]. A fair number of elements (including Cd, Cu, Hg, Pb, Zn) become volatile as halogenide (chlorides and bromides mainly); their volatilization evolves with temperature, supply of Cl and/or Br and depends also on the presence of oxidizing vs. reducing conditions.

In few cases, successful efforts were made to re-disperse the active phases of sintered catalysts. Hsu and Teng [306] showed that re-dispersion of Cu aggregates is feasible during the regeneration of (some) thermally deactivated catalysts. Treatment with a HNO<sub>3</sub> solution first dissolves and then redistributes these Cu aggregates, thoroughly regenerating the thermally deactivated catalyst. Likewise, Figueiredo, J.L. [307] shows that platinum crystallites cluster to aggregates at high temperature; yet, the platinum can be re-dispersed by creating oxychloro-platinum complexes during decoking. Indeed, Pt can form platinum oxychlorinated compounds and these can re-disperse on the surface, thus regenerating catalytic activity, if deactivated catalyst is simultaneously exposed to  $O_2$  and to HCl and to CCl<sub>4</sub>.

#### 6.3. Poisoning

Catalyst poisoning is essentially due to often irreversible adsorption of reactive elements or compounds, condensing or adsorbing onto the catalytic surface and/or to the occurrence of subsequent chemical reactions that form stable and catalytically less

or even inactive compounds. There are many possible mechanisms for deactivation by poisoning: a poison may simply clog pores or block active sites by irreversible reaction, or it may alter the adsorptivity of other species through electronic effects [38]. Poisons also can modify the chemical properties of the catalytically active elements. New stable and immobile compounds may be formed on the catalyst surface, resulting from the reaction of poisons with certain surface species. Investigations of catalytic oxidation of chloroaromatics here mainly focus on Cl-poisoning, since the Cl species produced during the decomposition of chloroaromatics can cause catalyst deactivation.

The deactivation of noble metal- and transition metal oxide- based catalysts caused by Cl-poisoning has been extensively studied. Because of the strong interactions between noble metal and chlorine, chloride species are formed during the reaction and then cover the active sites [134, 191, 192]. Among the transition metal oxides,  $MnO_x$ ,  $CrO_x$  and  $CeO_2$  all suffer badly from Cl-poisoning problems, seriously restricting their potential application in treating Cl-containing pollutants.

During the catalytic oxidation of chloroaromatics, serious deactivation of supported  $MnO_x$  catalysts was observed and ascribed to the formation of chlorinated and oxychlorinated manganese species, which were less active catalytically and covered the active phases [70, 107, 231]. For example, ClMnO<sup>-</sup>, Cl<sub>2</sub>MnO<sup>-</sup>, and Cl<sub>3</sub>Mn<sup>-</sup> species were detected and their impact increased together with the Mn load, indicating that chlorine interacted more markedly with catalysts containing crystalline MnO<sub>x</sub> in high proportion [70]. In such cases, the activity of the catalysts can be partially recovered with oxygen by re-oxidation of MnO<sub>x</sub> and removal of Cl species at appropriately high temperature [86].

Also,  $CrO_x$  deactivates rapidly while decomposing chlorinated pollutants. The loss of

Cr following the formation of highly toxic chromium oxychlorides explains the reduced activity of the catalyst [139, 140, 215], and deactivation is irreversible. After reacting for 17 h the removal efficiency of perchloroethylene dropped from 98% to 53% and the Cr content of the catalyst dipped from 12.5 % to 7.5 % [139]. Fast deactivation of CeO<sub>2</sub> was observed due to its strong adsorption ability for inorganic chlorine species at < 400°C. Therefore, the stability of CeO<sub>2</sub> could significantly improve if any chlorine species adsorbing on CeO<sub>2</sub> surfaces were removed more rapidly. During the decomposition of chlorobenzene over [115-119] Mn- and [96, 121-123] Ru-doped CeO<sub>x</sub>-catalysts, the removal rate of Cl from the catalytic surface depends on additives as well as temperature. Normally, chlorine species are removed faster at high temperatures favoring the oxidation of HCl.

#### 7. Miscellaneous

This section considers the effects from adding strong oxidants, such as ozone or hydrogen peroxide, or of water vapor and NO to the reactor input flow, as well as the external energy from plasma to the destruction of chloroaromatics.

#### 7.1. Ozone – hydrogen peroxide

Ozone (O<sub>3</sub>) shows strong oxidation capabilities and generates several strongly oxidizing radicals, such as O<sup>•</sup> and O<sub>2</sub><sup>2<sup>-</sup></sup>. It is increasingly used for degrading organic contaminants in aqueous solution as well as for drinking water disinfection: unlike chlorine or hypochlorite (OCI<sup>°</sup>), ozone does not generate chlorinated by-products. In contact with catalysts such as MnO<sub>2</sub>, Fe<sub>x</sub>O<sub>y</sub>, etc., O<sub>3</sub> produces highly active oxygen species, significantly enhancing the activity and stability of catalysts, as well as completing the oxidation of any pollutants present [308, 309]. Among a number of metal oxides, MnO<sub>2</sub> decomposes ozone most actively [310]. Already below 150 °C, the reactive species produced during this decomposition significantly stimulate the

catalytic decomposition of various volatile organic compounds such as acetone, benzene, etc. [311-314].

Ozone proper reveals relatively low activity [130] (Figure 12). When it adsorbs onto transition metal oxide catalysts and decomposes, it forms active oxygen species, allowing oxidation to proceed at lower temperature [311, 315-317]. Some catalysts can decompose ozone already at room temperature and attain their highest conversion level or even complete decomposition of target compounds already at 120~150 °C. Further raising temperature reduces conversion, however, presumably because of faster recombination of oxygen radicals to  $O_2$  (Jin et al. [113]). Also Batakliev et al. [318] reported on the mechanism of O<sub>3</sub> decomposition on transition metal oxides: O<sub>3</sub> dissociates while adsorbing onto the catalytic surfaces, forming  $O_2$  and  $O^-$ . Then,  $O^-$  reacts with ozone to form  $O_2^{2^-}$  and  $O_2$ . Finally, the adsorbed  $O_2^{2^2}$  decomposes, liberating  $O_2$ . According to this mechanism, both  $O^2$  and  $O_2^{2-}$  species are key intermediates during the decomposition of  $O_3$  and directly involved in the catalytic ozone-assisted oxidation of chloroaromatics. According to Li et al. [315] peroxide species  $(O_2^{2^-})$  are the main active species in a range of 25-100 °C during the catalytic decomposition of ozone on MnO<sub>2</sub> surfaces [317], while other researchers [309, 319] indicate O<sup>-</sup> as most active oxygen species.

RIF



Figure 12. Monochlorobenzene conversion vs. reaction temperature (GHSV: 83 s<sup>-1</sup>; Monochlorobenzene: 115 ppm;  $O_3$ : 600 ppm).[130]

Figure 12 compares the effect of oxygen with that of ozone, in the presence or absence of iron oxide. Applying O<sub>3</sub> to the catalytic decomposition of chloroaromatics could significantly lower the activation energy as well as the required reaction temperature (to below 200 °C), greatly improving decomposition efficiency [111, 130]. In addition, the introduction of ozone on metal oxides could change the main molecular mechanism, from a Mars and van Krevelen towards a Langmuir–Hinshelwood mechanism: pollutant molecules adsorbed on the catalytic surface efficiently react with the oxygen radicals produced by O<sub>3</sub> decomposition following a Langmuir-Hinshelwood route [113, 114].

Wang et al. [184, 185] stated that ozone promotes the catalytic activity of  $MnO_2$  and  $Fe_xO_y$  for decomposing PCDD/F, reaching destruction efficiencies higher than 90 % at 180 °C; in the absence of ozone, this decomposition efficiency only attained 20% and 25%. Supplying O<sub>3</sub> significantly reduces residual compounds subsisting on the catalytic surface, especially at low temperature, thus compensating for the low decomposition efficiency of the catalysts alone.

During the catalytic decomposition of monochlorobenzene over Fe<sub>2</sub>O<sub>3</sub>, the conversion at 150 °C attained 91% in the presence of O<sub>3</sub>, against only 3% without O<sub>3</sub> [130]. Ji et al. [172] reported a decomposition efficiency of PCDD/Fs of 99% at 220 °C during catalytic ozonation over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>: the active oxygen species generated from O<sub>3</sub> accelerated the conversion of V<sup>4+</sup> to V<sup>5+</sup>. Also, the optimal temperature of the catalytic reaction with O<sub>3</sub> present can be adjusted, according to the activity of metal oxide catalysts for decomposing O<sub>3</sub>: the most active catalyst, MnO<sub>x</sub>, shows an optimal temperature of only 120 °C [113], against 240 °C for the less active CuO<sub>x</sub> catalyst [114].

Likewise,  $H_2O_2$  has been proposed for oxidizing PCDD/Fs. Watts et al. applied it for destroying OCDD in soil. Degussa invented and marketed a process for removing halogenated organic compounds from waste gases which, optionally, contain  $NO_x$ , especially waste gases from refuse incineration plants [320]. In another invention,  $SO_2$  -free gas is passed, in the presence of hydrogen peroxide, over a substantially inorganic solid contact catalyst, in particular pyrogenic or precipitated silica or aluminum silicate [321].

#### 7.2. Effect of water

The effect of water on supported  $V_2O_5$  catalysts has been widely investigated. The molecular structure of surface  $VO_x$  species generally varies in the presence of water, following the formation of surface hydroxyl groups, i.e., V-(OH)<sub>2</sub> and V-OH [322-326]. The Raman shift of terminal V=O to lower wavenumbers suggests that this effect becomes more pronounced at either lower temperature or rising  $VO_x$  loading [219].





Moreover, isotope exchange experiments established that vanadyl oxygen (V=O and V-O-V) exchanges oxygen with water vapor more readily than with gaseous oxygen [219, 327]. Water molecule dissociates on  $V^{3+}$  sites, creating OH species (Figure 13). Subsequent re-oxidation by gas-phase oxygen forms O=VO<sub>2</sub> (OH), containing both Brønsted acid sites OH and active V=O species that are more active than on the original dehydrated surfaces [326]. Since no structural changes could be observed in the bulk of the catalyst [143], the influence of water seems restricted to the catalyst surface.



Figure 14. Light-off curves for the oxidation of m-DCB (500 ppm m-DCB, 10% O<sub>2</sub>, GHSV 53,000 mL/g h or 23,000 h<sup>-1</sup>) over a 3.6 wt.%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst under dry ( $\blacksquare$ ) and wet conditions in the presence of 1.0 vol.% ( $\blacktriangle$ ), 2.5 vol.% ( $\diamondsuit$ ), and 5.0 vol.% ( $\boxdot$ ) H<sub>2</sub>O. [143]

Figure 14 shows some activation/deactivation effects on the removal of dichlorobenzene and depending on the concentration of water [143, 179, 226] and temperature [81, 143]. Similar trends were also observed in the removal of chlorobenzene and 1,3,5-trichlorobenzene [103]. Already at low temperature, positive effects from removing chloride species [81, 82,

143, 226] and carbonaceous deposits [143] from the catalyst surface become

noticeable. In the presence of relatively high concentrations of chlorine species on the catalytic surface these species competitively adsorb on active sites and decrease the available amount of chemisorbed oxygen [328]. Water removes these surface chlorines apparently via an exchange, such as  $H_2O + CI^{-} \leftrightarrow HCl + OH^{-}$ . The removal of surface chlorine also reduces the generation of polychlorinated by-products, especially for noble metal catalysts [24, 148]. Carbonaceous deposits building up on the catalyst cause catalyst deactivation; yet they can be suppressed or removed by hydrolysis.

At temperatures > 300 °C, the deposition of chlorides and the creation of carbonaceous species both decrease, because of an improved redox-ability of the catalyst. As a result, the effect of water on the removal of surface chlorine and carbonaceous species becomes negligible [143].

Contrasting with these possible promoting effects, the presence of water vapor may also cause inhibition: competitive adsorption between water and various surface species can reduce the interaction between the target pollutants and the active phases [81, 143, 148, 226, 249]. An important reduction in number of medium and strong acid sites is induced by feeding water [249]; this can be deleterious, because acid sites are the typical adsorption sites for pollutants. However, such deactivation is entirely reversible and, after ending water addition, the system in a few minutes returns to the performance recorded under dry conditions [143].

At high temperature, the hydrolysis of 1,2-dichlorobenzene may become competitive to its oxidation and different oxidation products are formed after addition of water [154]. Above 350 °C and up to 450 °C, the intensity of the characteristic bands, corresponding to surface phenolate species increased significantly. Conversely, already at 200 °C surface phenolate species are not distinctly observed under dry

conditions [76, 82-84]. Therefore, the reaction pathway could be modified due to water addition at higher temperature. Gonzalez-Velasco et al. [329] suggested that in excess of water hydrolysis becomes a dominant pathway in the catalytic decomposition of trichloroethylene.

### 7.3. Effect of NO<sub>x</sub>

During the conversion and oxidation of chlorobenzene on  $VO_x/TiO_2$  and  $VO_x-WO_3$  (MoO<sub>x</sub>)/TiO<sub>2</sub> catalysts Bertinchamps et al. [330] also investigated the influence of adding NO: in the presence of O<sub>2</sub>, NO improved chlorobenzene conversion; the effect was still larger when the catalyst contained either W or Mo. Thus, a mechanism explaining the positive effect of NO was proposed as follows:

- mainly on WO<sub>3</sub> and MoO<sub>2</sub>, NO is oxidized to NO<sub>2</sub>;
- the NO<sub>2</sub> formed assists O<sub>2</sub> in re-oxidizing vanadium oxides, accelerating the oxidation cycle (Figure 15).

This team also investigated the oxidation state of fresh and used vanadium catalysts, proving that NO<sub>2</sub> was more efficient than O<sub>2</sub> in re-oxidation, keeping vanadium at a higher oxidation state than in the fresh catalyst, as shown in Figure 16 [88, 249]. Also Xu et al. [89] found a positive effect of NO, during the oxidation of pentachlorobenzene.





Figure 16. Mean oxidation level of vanadium in the  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> catalyst, as a function of oxidant (NO, NO<sub>2</sub>, atomic O) concentration. [88]

#### 7.4. Non-thermal plasma

When a relatively high energy is applied to gas, the kinetic energy of electrons in gas molecules exceeds the ionization energy, required to produce plasma states. Such a state of a medium is composed of free electrons, radicals, positive and negative ions, apart from molecules. Some species (OH•, O•) are very active during the catalytic oxidation of environmental pollutants. According to the temperature correlations of electrons (T<sub>e</sub>), ions (T<sub>i</sub>) and neutral particles (T<sub>n</sub>), plasma is generally divided into thermal plasma, with T<sub>e</sub>  $\approx$  T<sub>i</sub>  $\approx$  T<sub>n</sub> [330, 331] and non-thermal plasma with T<sub>e</sub> >> T<sub>i</sub>, T<sub>e</sub> >> T<sub>n</sub> [333, 334].

In the last two decades, the application of non-thermal plasma (NTP) has seen extensive experimental explorations. The energy supplied to the system is almost completely consumed, while accelerating electrons so as to attain typical temperatures of 10,000–250,000 K (1–20 eV) [335], whereas the remaining gas medium rests at room temperature. Thus, a NTP operates under ambient conditions, yet still suffers from low energy efficiency, low mineralization degree and generation of additional

pollutants (SO<sub>2</sub>,  $H_2S$  and  $NO_x$ ) [336].

Compared with NTP alone, a combination of NTP and catalysis could result in higher energy efficiency and mineralization rates and lower by-product yields, during the decomposition of VOCs [337]. Karuppiah et al. [338] reported a 100% conversion selectivity to  $CO_2$  at 260 J L<sup>-1</sup> during the removal of chlorobenzene with an AgO<sub>x</sub>/MnO<sub>x</sub> catalyst.

NTP combined with the catalytic removal of trichloroethylene, benzene and toluene was reviewed in [337, 339, 340]. Figure 17 illustrates schematics showing the two major options to combine plasma and catalytic techniques, with the catalyst situated either within (Figure 17a) or after (Figure 17b) the plasma discharge zone.



Figure 17. Two configurations combining plasma and catalyst: a. in-plasma and b. post-plasma positioning. The most common catalyst insertion methods are summarized for the in-plasma configuration (c). [337]

In summary [337, 341-344], combining non-thermal plasma and catalysis leads to the following potential improvements:

Introducing a catalyst into the plasma system may influence both the type and quality of plasma discharge, transform the distribution of accelerated electrons, and facilitate the generation of new reactive species (e.g. O<sub>2</sub><sup>-</sup> formed from the O<sub>3</sub> decomposition on the surface of catalysts).

- Adsorption of pollutants on the catalysts increases their concentration and their retention time.
- The plasma induces physico-chemical changes in a catalyst, including the dispersion of active phases, their oxidation state and specific area.
- Plasma can thermally activate the catalyst (hot spots)
- Catalytic activation can also be achieved by photon irradiation.

During the reactions, the in situ  $O_3$  decomposition over the applied catalysts plays a dominant role [338, 340].

### 8. Future directions for research on catalytic oxidation

There are still many issues to be resolved to meet the stringent emission standards in a cost-efficient and effective manner. First, the current understanding of the mechanisms of catalytic oxidation process is far from complete. Too little is known about reaction pathways at the molecular level, the interaction of the different components of the catalyst with the reactants, etc. Various research studies still remain at the stage of experimental tests and it is difficult to scrutinize the result thoroughly as well as theoretically and to conduct deeper research that allows improving the physical and chemical properties of catalysts. Moreover, to lessen the catalyst deactivation caused by ash and sulfates, the catalytic systems are congruently placed after the filter where temperature is typically below 150 °C. So the enhancement of catalytic activity at low temperature is still crucial. In addition, since catalyst deactivation is inevitable, finding how to reduce the cost of catalyst replacement is of vital importance.

Regeneration methods need to be studied further to achieve high recovery efficiency.

On the other hand, research on in situ regeneration is also very attractive, since it can greatly decrease operating cost. Due to high operating and maintenance cost, many plants are averse to install catalytic systems. Therefore, the study to improve catalytic systems and prolong their guaranteed lifetime and decrease their replacement cost is also very important.

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Figure 1. Process flow diagram of the deNO<sub>x</sub> at the MSWI of Ghent. Figure 2. Reaction mechanism for the oxidation of chlorinated benzenes  $V_2O_5/TiO_2$  catalysts.

Figure 3. The turnover frequency (TOF) during the total oxidation of formaldehyde on Pt/TiO<sub>2</sub> as a function of Pt-particle size (calculated from CO chemisorption). Figure 4a: Hydrogenation energies  $E_{hydrogenation}$  and their relationship with the corresponding LUMO energies  $E_{LUMO}$ . b: LUMO energies of the oxidized state and HOMO energies of the reduced state of oxides in"Zone A of a. Black solid symbols represent the LUMO energy of the oxidized state, blue hollow symbols show the HOMO energy of the reduced state. Copyright 2014 ACS Publications.

Figure 5. (a) Temperature for reaching 80% 1,2-dichlorobenzene conversion (**■**) and  $CO_x$  selectivity (**▲**) at this 80% conversion level, as a function of the theoretical  $VO_x$  density for TiO<sub>2</sub>/WO<sub>3</sub> based catalysts. (b) Product selectivity for samples of different vanadium content.  $V_2O_5 = 1.8$  wt.% (**▲**),  $V_2O_5 = 3$  wt.% (**●**) and  $V_2O_5 = 5$  wt.% (**♦**) (CO<sub>x</sub> solid line; dichloromaleic anhydride dotted line).

Figure 6. Reaction mechanism for oxidizing o-dichlorobenzene on vanadium supported catalysts in presence of [A] a high number of Brønsted acid sites; [B] prevailing Lewis acid sites.

Figure 7. SEM images of (a, b) rod-like MnO<sub>2</sub>, (c, d) wire-like MnO<sub>2</sub>, (e, f) tube-like MnO<sub>2</sub>, and (g, h) flower-like Mn<sub>2</sub>O<sub>3</sub>. Copyright 2012 ACS Publications.

Figure 8. (a) Distribution of M-O bond lengths of  $CeO_2$ ,  $RuO_2$  and  $Ce_{28}Ru_4O_{62}$  (M = Ru, Ce); (b) Distribution of M-O bond lengths of  $CeO_2$ ,  $MnO_2$ , PdO,  $Ce_{28}Mn_4O_{62}$  and  $Ce_{27}Mn_4Pd_1O_{61}$  (M= Ce, Mn and Pd). Copyright 2010 ACS Publications.

Figure 9. SEM and TEM images of  $V_2O_5/TiO_2$ -CNT composites: (a)  $V_2O_5/TiO_2$ , (b)

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-(0.8wt.%)CNTs (c) V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-(5.1wt.%)CNTs, (d)

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-(6.2wt.%)CNTs, (e) V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-(8.6wt.%)CNTs, (f)

V2O5/TiO2-(8.6wt.%)CNTs after 150 h activity test, and (g) TEM image of

V2O5/TiO2-(8.6wt.%)CNTs. Copyright 2011 ACS Publications.

Figure 10. FESEM images of (a) pristine OMS, (b) Cu(0.2)-OMS, (c) Cu(0.4)-OMS, and (d) Cu(0.6)-OMS. The catalysts denoted as Cu(0.2)-, Cu(0.4)-, and Cu(0.6)- with the number referring to the Cu/Mn molar ratio in the precursor solution of 0.2, 0.4, and 0.6, respectively.

Figure 11. SEM images of (a)  $Fe_2O_3$ , (b) FeCa5, (c) FeCa10 and (d) FeCa20 catalysts. In FeCa5, FeCa10, and FeCa20 the number refers to the nominal content of Ca, i.e. 5, 10, and 20 mol %, respectively.

Figure 12. Monochlorobenzene conversion vs. reaction temperature (GHSV: 83 s<sup>-1</sup>; Monochlorobenzene: 115 ppm;  $O_3$ : 600 ppm).

Figure 13. Exchange of lattice oxygen with adsorbed  $H_2^{18}O$ , involving a redox cycle. Copyright 2010 ACS Publications.

Figure 14. Light-off curves for the oxidation of m-DCB (500 ppm m-DCB, 10%  $O_2$ , GHSV 53,000 mL/g h or 23,000 h<sup>-1</sup>) over a 3.6 wt.%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst under dry

(**•**) and wet conditions in the presence of 1.0 vol.% (**•**), 2.5 vol.% (**•**), and 5.0 vol.% (**•**)  $H_2O$ .

Figure 15. Chlorobenzene oxidation in the absence (A) or presence (B) of NO. Figure 16. Mean oxidation level of vanadium in the  $V_2O_5$ -WO<sub>3</sub>/TiO<sub>2</sub> catalyst, as a function of oxidant (NO, NO<sub>2</sub>, atomic O) concentration.

Figure 17. Two configurations combining plasma and catalyst: a. in-plasma and b. post-plasma positioning. The most common catalyst insertion methods are summarized for the in-plasma configuration (c).

- Industrial installations for eliminating dioxins from flue gas. ٠
- Mechanisms of catalytic oxidation of chloroaromatics. ٠
- Catalyst classification and adaptation.
- Catalyst deactivation and possible regeneration. ٠
- Miscellaneous methods to improve the catalytic oxidation process. •

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