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Review

General and Prospective Views on Oxidation Reactions in Heterogeneous Catalysis

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Abstract: In this short review paper we have assembled the main characteristics of partial oxidation reactions (oxidative dehydrogenation and selective oxidation to olefins or oxygenates, as aldehydes and carboxylic acids and nitriles), as well as total oxidation, particularly for depollution, environmental issues and wastewater treatments. Both gas-solid and liquid-solid media have been considered with recent and representative examples within these fields. We have also discussed about their potential and prospective industrial applications. Particular attention has been brought to new raw materials stemming from biomass and to liquid-solid catalysts cases. This review paper also summarizes the progresses made in the use of unconventional activation methods for performing oxidation reactions, highlighting the synergy of these technologies with heterogeneous catalysis. Focus has been centered on usual catalysts activation methods but also on less usual ones, such as the use of ultrasounds, microwaves, grinding (mechanochemistry) and photo-activated processes, as well as their combined use.

Keywords: heterogeneous catalytic oxidation, gas-solid, liquid-solid, partial and total oxidation, biomass based raw materials, activation methods

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1. Introduction

Oxidation reactions cover a large part of the heterogeneous catalysis field, and concern selective (or partial) and total oxidations of organic compounds and a large part of heterogeneous catalytic industrial reactions, and processes, mainly in petrochemistry. This field involves both gas-solid and liquid-solid media, the solid being the catalyst.

The advent of nanoscience has promoted bottom-up over top-down strategies. Nanocrystals with sizes of only a few nanometres present high catalytic efficiencies due to higher surfaces available to reactants. They are often supported on metal oxides or on active carbons, which may lead to a determining role in the synergistic activation of substrates, in electron conductivity changes, in the enhancement of redox reactions, in improving thermal conductivity, particularly useful for exothermal reactions, which is important for selective oxidation reactions in industrial processes. The activity, selectivity, resistance to deactivation, and ability for regeneration are properties which are looked for their usefulness and their use industrially. The catalysts covered in this review are mainly nanostructured single and mixed metal oxides or the corresponding supported counterparts, as well as noble metals such as silver for epoxidation reactions, Pt for total oxidation reactions or gold and its alloys for liquid phase aerobic selective oxidation reactions (glycerol or allyl alcohols conversions). Enzyme-based catalysts also constitute a promising biocatalysis approach for future developments, whereas biomass and biomass-derived products constitute new raw materials resources for future applications, mainly in liquid phase media.

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Selective oxidation reactions are involved in many industrial processes, such as those leading to aldehydes, carboxylic acids or nitriles in petrochemical industries, while total oxidation is used mainly in suppressing atmospheric pollution, as well as for pollutants degradation in liquid phase in wastewater treatments.

This review is aimed at providing a concise and representative coverage of recent developments in the field of partial and total oxidation reactions in gas phase and liquid phase. The review is organized in two main sections. The discussion starts with the case of selective oxidation reactions in gas phase (2.1.), then in liquid phase (2.2.). A special sub-section has been dedicated to the beneficial role of unconventional activation methods (*i.e.* sonochemistry, microwave, mechanochemistry, electrochemistry and photochemistry) in enhancing liquid phase selective catalytic oxidation reactions, through representative cases (2.3). Then the discussion moves to the use of such eco-friendly physical activation technologies for the development of greener and cost-effective synthetic routes for designing catalytic materials with controlled characteristics and improved catalytic properties for the selective oxidation of alcohols to the corresponding aldehydes or carboxylic acids (2.4). The second main section is dealing with total oxidation reactions in gas phase and liquid phase. At this point, gas phase-solid catalyst total oxidation for depollution treatment is presented with a large part devoted to the case of atmospheric pollutants, such as industrial volatile organic compounds (VOCs) and/or highly diluted VOCs. Hybrid treatments combining catalytic oxidation with other technologies (*e.g.* light, ozonation, non-thermal plasma) have also been developed. The review ends up with the degradation of organic pollutants in liquid phase with a focus on advanced oxidation processes.

Since our analysis cannot be overlong, the authors hope to provide informative and insightful representative examples on partial and total oxidation reactions in heterogeneous catalysis. Readers are also encouraged to refer to the cited review articles for additional in depth information.

2. Selective Oxidation Reactions in Gas Phase and Liquid Phase

2.1. Gas Phase-Solid Catalyst Selective Oxidation Reactions

This domain has led to the development of many industrial processes, mainly in the petrochemistry field, since the 1960s with the use of bismuth molybdate based catalysts for the oxidation of propene to acrolein and its ammoxidation to acrylonitrile by Sohio researchers [1]. This process has been recently reviewed by Brazdil [2,3], whereas the whole heterogeneous catalytic selective oxidation field has been reviewed recently by López Nieto [4] and Dagnan [5]. Such reactions proceed, majority of the time, by the *so-called* Mars and van Krevelen (MvK) [6] redox-type mechanism schematized below in equations {1} & {2} and was found to obey the 7 pillars rule as defined by Grasselli [7,8] namely:

- Nature of lattice oxygen anions, being either nucleophilic (partial oxidation) or electrophilic (total oxidation)
- Redox properties of the metal oxide (reduction of the cation with subsequent removal of lattice oxygen anions and their rapid reinsertion by oxygen from the gas phase)
- Host structure which should permit redox mechanism to take place, with lattice oxygen anions removal and its reinsertion, without the collapse of the crystalline structure
- Phase cooperation in multicomponent catalyst or supported catalyst (epitaxial growth and synergetic effects), which facilitates electron transfer, thus electrical conductivity, and lattice oxygen anions mobility and thus the MvK redox mechanism.
- Multifunctionality (e.g., α-H abstraction and O-/NH- insertion)
- Active site isolation, to avoid a too high lattice surface oxygen anions mobility and thus over-oxidation of the products to CO_2.
- M-O bond strength, to be not too weak (total oxidation) nor too strong (inactivity) (Sabatier's principle).

This MvK mechanism is involved when the catalyst contains cations with a variable oxidation state, such as Ce, Co, Cr, Cu, Fe, Mo, Nb, Ni, Ti, V or W according to:

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$$2[CatO] + R–CH_3 \rightarrow 2[Cat] + R – CH{=}O + H_2O \quad \{1\}$$
$$2[Cat] + O_{2(gas)} \rightarrow 2[CatO] \quad \{2\}$$

In this scheme, [CatO] refers to the oxidized surface and [Cat] to its reduced state. If r_{red} is the rate of reduction of the catalyst by a hydrocarbon (HC, as R-CH_3) and r_{ox} the rate of its re-oxidation by gaseous oxygen, resulting in the oxygenated product R–CH=O, the kinetic equation can be written as:

$$r = k_{ox}\, k_{red}\, PO_2^{\,n} P_{HC} / \{k_{ox}\, PO_2^{\,n} + k_{red}\, P_{HC}\}.$$

At the steady state, $r_{red} = r_{ox}$ or $k_{red}\, P_{HC}(1-\theta) = k_{ox}\, P_{O2}\, \theta$ with P_{HC}, P_{O2} are the partial pressures of HC and O_2 and k_{red}, k_{ox} the rate constants of reduction of catalyst (1st step equation {1}) and of its reoxidation by O_2 (second step equation {2}), with a concentration of reduced (θ) and oxidized (1-θ) sites of the catalyst surface. The relative rate values are important to determine the selectivity, since the reaction necessitates lattice oxygen anions, which are incorporated into the reactant molecule {1}, whereas the corresponding vacancy created is replenished by gaseous oxygen in the re-oxidation step {2}.

It is noteworthy that, if one has $k_{red}\, P_{HC} >> k_{ox}\, P_{O2}$, the surface reoxidation is the rate-determining step (rds), whereas if $k_{red}\, P_{HC} << k_{ox}\, P_{O2}$, the surface reduction is the rate-determining step. It follows that the redox properties of the catalyst surface is quite important and determining for its catalytic properties and can be characterized by temperature programmed reduction (TPR) and oxidation (TPO) measurements.

The main catalysts used industrially [9] are bismuth molybdate-based oxides since the pioneered work by researchers at Sohio in the 1960s, (e.g. multicomponent catalysts as BiMo-O + $CoFeMoO_4$) for propene oxidation/ammoxidation to acrolein, acrylic acid/acrylonitrile ; vanadyl pyrophosphate $(VO)_2P_2O_7$ catalyst, designated as VPO, for butane direct oxidation to maleic anhydride ; MoVTe(Sb)Nb-O oxides (in particular those referred to as M1 and M2 phases) for direct conversion of propane to acrylonitrile or acrylic acid ; iron phosphate-based catalysts for oxidative dehydrogenation of isobutyric acid to methacrylic acid ; iron molybdate ($FeMO_4$) for oxidation of methanol to formaldehyde ; V_2O_5/TiO_2 for o-xylene oxidation to phthalic anhydride ; benzene oxidation to phenol on titanosilicalite MFI zeolite (TS1) ; MoVNb-O for ethane oxydehydrogenation (ODH) to ethene or its oxidation to acetic acid. For the selective oxidation of light alkanes vanadium element appears as a major constituent of many active catalysts [10,11].

Recently, new mixed metal oxides have been proposed for gas phase selective oxidation reactions. For instance, bronzes A-M-B-O (A= NH_4^+, H^+, alkali or alkali-earth cations; M= Mo and/or, W; B= V and/or Nb) with different types of channels in the ab plane, and grown along the c plane, have been proposed [12] for the ODH of ethane to ethene and selective oxidative of ethanol to acetaldehyde [13]. Oxydehydration of glycerol to acrylic acid [14] was studied on a series of $Mo_3VO_x/H_4SiW_{12}O_{40}/Al_2O_3$ catalysts and applied to one-step reaction. It was found that acetic acid was produced in parallel with acrylic acid, with similar yield, when adjusting Mo_3VO_x content in the catalysts. Crystallinity of Mo_3VO_x was observed to increase with calcination temperature from 350 to 650°C, while a large amount of $(V,Mo)O_x$ hetero-polyoxo mixed oxides was formed above 550 °C. The Keggin structure of $H_4SiW_{12}O_{40}$ was observed to dissociate near 450 °C, causing the formation of various WO_x species, while the yield of acrylic acid dropped and acrolein formation reached its maximum value, whereas the yield of acetic acid did not change appreciably. These temperature effects show how important are activation conditions. In the one-step oxidative conversion of glycerol, both acidic and redox properties of catalysts were shown to have to be finely tuned. Moreover, it was also reported that both W–V–O and W–V–Nb–O catalysts are active for methanol oxidative gas-phase transformation to formaldehyde and dimethyl ether (DME). It was shown that there exists a relation between the reaction conditions and catalyst features needed to convert oxygenated molecules by means of direct processes, using a single multifunctional catalyst. Catalytic performance of lanthanum vanadate ($La_{0.1}V_{0.9}O_x$) catalyst in the ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyarazine (CP) has also been investigated [15].

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The recent developments in the field of catalytic partial oxidation of ethane to oxygenated products have been comprehensively reviewed [16]. Moreover, the comparative catalytic oxidation of alcohols in both gas phase and liquid phase over size-controlled Pt nanoparticles was reviewed very recently [17].

2.2. Liquid Phase-Solid Catalyst Selective Oxidation Reactions

From the point of view of chemicals and energy resources, and with the objective of reducing our carbon footprint, utilization of resources other than fossil resources is essential for overcoming environmental issues and for the elaboration of a more sustainable world. One candidate for such resources is biomass, in particular sugars and lignocellulosic biomass (lignin, hemicellulose and cellulose fractions). Conversion of biomass and biomass-derived products has been studied extensively in recent years towards the production of high added value products. Biodiesel synthesis and utilization of glycerol, its major by-product, are also important topics, already largely studied worldwide in the past ten years. It has indeed been widely reported that, for reducing the carbon footprint of fuels, biodiesel represents an interesting and promising option for theoretical carbon zero overall consumption reactions. The biodiesel production trend leads to large amounts of glycerol, co-produced by conventional trans-esterification reaction used to synthesize the bio-fuel, which has significantly impacted the glycerin market, resulting in a lowering of its price, and has made glycerol a low-cost raw material for conversion into different chemicals with higher economic value and a key element for developing bio-based chemical industry [18]. Currently, only one process has been industrialized for biodiesel production on $ZnO-Al_2O_3$ catalysts.

Among the several options for glycerol conversion, a great attention has been paid to its dehydration into acrolein [12]. Acrolein is produced primarily by the gas-phase oxidation of propylene, as reminded above. However, as the use of propylene derivatives, particularly for the synthesis of polypropylene, has largely increased in the last decade, and, since this trend is likely to continue in the foreseeable future, the availability and cost of propylene is going to increase. Catalysts and processes have then been developed for the direct conversion of glycerol to acrolein by simple dehydration on acid catalysts [19]. However, in such processes, the catalysts face two major difficulties: (i) there is a more or less rapid deactivation; (ii) selectivity is limited to less than 80%. There is thus a need for the development of novel routes for the production of acrolein. One approach could involve the conversion of allyl alcohol, which could be produced in an initial step either by fermentation or through the use of processes such as the dehydration of 1,3-propanediol or the dehydration/oxidation of glycerol [19]. Glycerol or allyl alcohol partial oxidation to dihydroxyacetone to acrylic acid have also been largely studied and published in the open literature [20-24]. Oxidehydration of glycerol into acrylic acid has been reported using multifunctional catalysts able to carry out in a single-step transformation its dehydration to acrolein and further oxidation into acrylic acid, both in gaseous and liquid phases [17]. Vanadium-containing tungsten oxide bronzes ($W_{1-x}M_xO_z$ catalysts; $0 < x < 0.33$, M: Nb, V) constitute one of the most promising catalytic systems to perform the one-pot oxidehydration of glycerol to acrylic acid [25-27]. An enhanced catalytic behavior for KIT-6 mesoporous silica supported $W_{1-x}M_xO_z$ catalyst has been observed for that reaction, in which an increase in the yield to acrylic acid (31 %) is observed compared with the unsupported catalyst (19 %). This improvement has been ascribed to both the effect of the support on the size of bronzes and the specific vanadium species present in these supported catalysts. In this way, bulk W-V-O bronze shows a higher concentration of medium-high strength acid species on the surface, which substantially decrease when supporting it on the mesoporous silica.

The liquid phase selective transformation of oxygenated compounds in aqueous effluents (obtained by phase separation after biomass fast pyrolysis processes) is an important target in the development of biorefineries. For instance, selective oxidative esterification of furfural with methanol to methyl 2-furoate for flagrance was studied on gold supported on different supports, such as ZrO_2, CeO_2, TiO_2 or Fe_2O_3 [28-30]. Furfural has been recognized as one of the top value-added biomass-derived chemicals [31], which is due to already available commercial applications in the chemical industry.

Oxidative esterification of biomass-derived furans, including furfural and 5-hydroxymethylfurfural (HMF) to the corresponding esters, was also successfully performed over non-precious metal catalysts, namely cobalt-based carbon-supported catalysts obtained after pyrolysis of a molecularly defined Co complex adsorbed on activated carbon [32]. Among the biomass-derived chemical building blocks, 2,5-furan dicarboxylic acid (FDCA) is also considered as a key near market platform chemical, because it may replace terephthalic acid in various polyesters. The traditional synthesis of FDCA from HMF requires harsh and corrosive conditions and poor atom efficiency due to waste generation during product purification. As a greener alternative route, it was shown that Au/hydrotalcites can selectively drive HMF aqueous phase aerobic oxidation to FDCA at low temperature, but only with high gold surface concentration [33]. Such aqueous phase aldehyde and alcohol cascade oxidations could also be carried out effectively over mixed MnxFey oxide catalysts under mild reaction conditions [34].

The production of value-added organic acids by selective oxidation of biomass resources is also of great importance in the current chemical industry. Transition metal single oxides, such as CuO, have been used for the selective conversion of glucose to lactic acid and acetic acid under hydrothermal conditions [35]. In addition to the use of single oxides, lactic acid can be produced by conversion of a variety of cellulosic biomass over mixed metal oxides of the perovskite-type as well [36]. The authors have shown that the redox properties of the $LaCoO_3$ catalyst, distinct from that of the acid-base prevailing catalysts, are key parameters in the conversion of glucose, xylose and cellulose to lactic acid in water under subcritical conditions. In a very recent study, it was reported that the proper combination of solvents and solid catalysts can improve the production of di-acids from biomass [37]. The use of γ-valerolactone (GVL), as renewable co-solvent, along with titanium silicalite (TS-1) as catalyst and H_2O_2 as the oxidant, allowed the authors to generate furfural and its direct upgrading to maleic acid both in high yield at low reaction temperatures. Deactivation of the catalyst was prevented thanks to the presence of GVL as co-solvent by avoiding insoluble heavy by-products deposits on the surface of TS-1, substantially improving its long-term stability. Hence the catalyst could be reused for 17 successive runs without detectable deactivation, whereas deactivation occurred when the reaction was performed in water. Several perovskites metal oxides ($LaMnO_3$, $LaCoO_3$, $LaFe_{1-x}Cu_xO_3$, etc) were also shown to efficiently catalyze the wet aerobic oxidation of lignin to aromatic aldehydes [38].

Wide researches are performed worldwide trying to discover new catalysts able to give better reaction yield or even new catalytic reaction. In addition to many metal oxide catalysts, one may cite poly-oxometallates (POMs) of Keggin or Dawson structures, porous metal oxides (whatever micro- or meso-porous materials), such as the MOFs family (Figure 1) as tentative new catalysts for epoxidation reactions in liquid phase [39] and even inclusion of POM in MOF has attracted much recent attention [40] in selective oxidation reactions in liquid phase [41-43].

Regarding the nature of the oxidizing agent and in particular the case of hydrogen peroxide, its direct synthesis is a dream reaction (search for the Graal!!) in the field of selective oxidation reactions and green chemical synthesis. In a recent report, direct synthesis of H_2O_2 in water over Pd/TiO_2 catalysts was examined in a continuous flow reactor setup at ambient temperature and elevated pressures [44]. Under reaction conditions, the supported Pd nanoparticles were inactive when covered by chemisorbed oxygen, but when hydrogenated they were able to form palladium hydride, as revealed by operando XAS studies. Such hydride is able to form H_2O_2 for H_2/O_2 ratio < 2.0 under pressure (~1 MPa), conditions valid to form the α-PdH_x phase rather than the β-Pd hydride which favors the formation of water. Such results will undoubtedly prompt the search for the rational design of catalysts and the optimization of the process parameters for making the direct synthesis of H_2O_2 viable.

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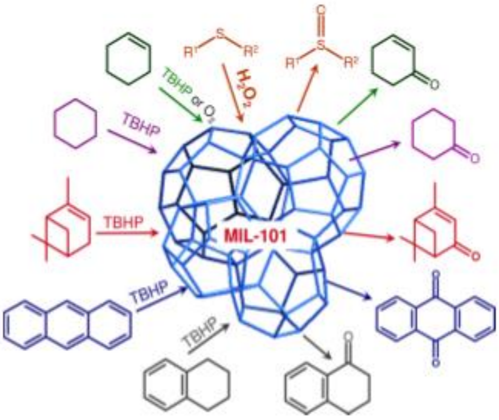

Figure 1. Oxidation reactions performed on Cr-MIL-101 MOF catalysts [41].

Although major industrial processes have been discovered and developed by the second half of last century, progress is still needed, and the major challenges for the future are to reach 100% selectivity and to use less energy. In this respect, unconventional activation methods based on ultrasound (US) and microwave (MW) irradiations, ball milling (reactive grinding), electrochemical and photo-activated processes, are viewed as "*Green Chemistry*" approaches to increase reaction rates, shorten reaction times while enhancing yields and selectivities. These aspects will be discussed in the following section.

2.3. Unconventional Activation Methods for Liquid Phase Selective Oxidation Reactions

Unconventional activation methods are non-thermal technologies that do not involve any external source of heating. Hence, the chemical reaction can be activated either by (1) the technology itself through the action of light, pressure, electric field, waves, etc. or (2) by the heat generated *in situ*. Such eco-friendly physical activation methods offer challenging opportunities for developing clean, selective and energy-efficient synthetic strategies both for the production of high value-added compounds [45,46] or for pollutant abatement. Here, the synergy of these technologies with catalysis for selective oxidation reactions in liquid phase is emphasized through selected representative literature studies. Sonochemistry, microwave, mechanochemistry, electrochemistry and photochemistry have been chosen for the discussion.

Sonochemistry is a field of chemistry based on energy delivered by power ultrasound. The ultrasonic effects originate from the cavitation phenomenon, namely the rapid nucleation, growth and collapse of gaseous bubbles generated in the sonicated liquid. This sudden collapse is responsible for chemical effects (formation of radical species) and mechanical effects (shear forces, microjets, shock waves), leading to the acceleration of organic transformations thanks to the mass transfer effect induced by sonication. Cavitation depends on external parameters such as the frequency, intensity, nature and temperature of the sonicated solvent, geometry of the reactor, etc.

The combination of ***ultrasonic waves*** and heterogeneous catalysts has proven to be a useful choice in selective conversions of organic substrates to value-added chemicals. The coupling of a nanostructured Co_3O_4 catalyst with ultrasonic irradiation (19.95 kHz) enables the selective oxidation of a lignin-derived compound (vanillyl alcohol) to the corresponding aldehyde (vanillin) under milder conditions than under conventional heating in the absence of US irradiation [47]. The US-assisted reaction with H_2O_2 as O-donor and water as solvent at ambient pressure proved to be faster (4x), more selective (2.3x), more performant (2.7x) and more energy efficient (8x) than the reaction carried out under silent conditions. The results have been ascribed to enhanced chemical effects (production of HO• through *in situ* formation of H_2O_2 in the sonicated water) and physical effects (increased mass transfer) promoted by ultrasound on the catalyst surface. In another study, the selective conversion of a variety of substituted and cyclic alcohols and alkenes to the corresponding aldehydes, ketones and epoxides has been conducted in CH_3CN in the presence of

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multi-walled carbon nanotubes supported on TiO_2 in an ultrasonic bath working at 40 kHz and 250 W [48]. Excellent yields were obtained within 15-30 min due to synergistic effects between the hybrid nanocatalyst and ultrasonic irradiation. More information about the coupling of ultrasonic waves and metal-based catalysts in targeted organic compounds synthesis, including oxidation reactions, can be found in the review of Domini *et al*. [49].

Among the physical activation technologies able to promote fast chemical transformations, microwave is probably the most popular one. By absorbing the MW energy, the reaction mixture undergoes a rapid internal heating through the interaction of the electromagnetic irradiation with the molecules contained in the mixture.

In a recent work, the direct production of vanillin and vanillic acid from wood particles has been carried out in a MW-assisted reaction using CuO and hydrogen peroxide [50]. The effects of ***electric and magnetic fields*** on the reaction yields have been determined by using a cavity resonator, which can separate both fields. The reaction has also been performed in the same reactor under the same heating conditions but under conventional heating for comparison purposes. Under MW heating at 180°C for 10 min, the yield to vanillin and vanillic acid was three times higher than that obtained without MW irradiation. The higher production rate observed in the MW-assisted reaction is due to both electric and magnetic fields (lower apparent activation energy values) with a slightly more prominent effect of electric fields, highlighting the MW-sensitive character of this reaction, as compared to conventional heating (Figure 2).

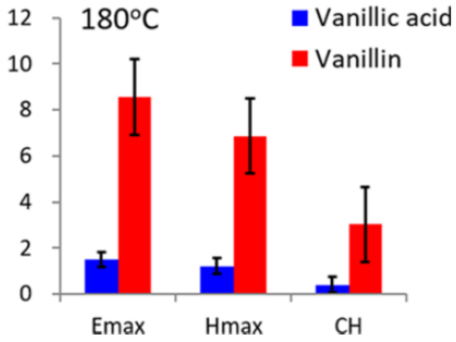
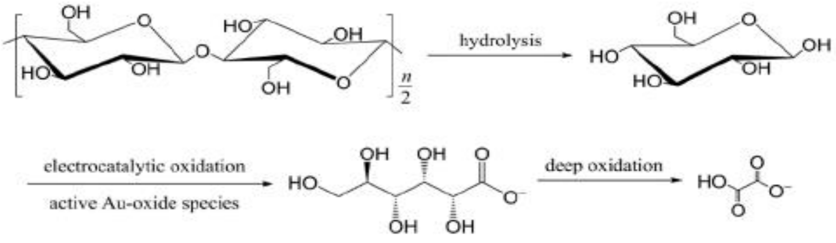


Figure 2. Comparison of the yields to vanillin and vanillic acid by microwave electric (E_{max}) and magnetic (H_{max}) effects and conventional heating (CH) in a cavity perturbation heating system, adapted from [50].

Mechanochemistry also represents an alternative solvent-free route to traditional methods for selective transformation reactions. According to the IUPAC definition, mechanochemistry is the branch of solid-state chemistry where a chemical reaction is induced by the direct absorption of mechanical energy [51]. In a mechanochemical process, intramolecular bonds are broken during the grinding or ball milling of the reactants (mechanical action) followed by further chemical reactions. The selective oxidation of a broad set of primary and secondary benzyl alcohols to the corresponding aldehydes and ketones has been recently performed under solvent-free ball milling conditions with no trace of over-oxidation carboxylic acid products [52]. Under mechanical activation conditions with zirconia milling balls, higher yields and rates could be obtained than with the classical TEMPO-based oxidation reaction. This study emphasizes that reactive grinding constitutes a viable physical activation technology for the solvent-free conversion of a library of alcohols to aldehydes, provided the milling time is adequately defined. Otherwise, the decomposition of the desired products can occur under prolonged milling times due to the mechanical action.

Electrocatalytic oxidation is another alternative approach for biomass conversion due to its high reaction activity, low energy consumption and environmental compatibility [53]. For instance, a variety of carbohydrates could be transformed effectively in electrochemical reactors under mild reaction conditions for the production of high value-added feedstocks. The electrocatalytic selective oxidation of cellulose to gluconate was reported on a carbon aerogel (CA) supported gold nanoparticles as anode in an alkaline medium [54]. Dissolution of cellulose in the NAOH solution promoted its hydrolysis, prior to its electrocatalytic conversion to gluconate on Au/CA anode or eventually to oxalate for prolonged electrolysis times (Scheme 1).



Scheme 1. Electrocatalytic oxidation of cellulose to gluconate [54].

Photocatalysis can also be used for the transformation of organic compounds into valuable products in liquid phase. The mechanism of this reaction follows three steps: i) under UV-light illumination, the absorption of photons by the photocatalyst creates an electron–hole (e^-h^+) pair when the photon energy is larger than that of the band gap, ii) this e^-h^+ pair migrates to the surface and are trapped by OH surface groups forming hydroxyl ($HO^{\bullet}$), hydrosuperoxide ($HO_2^{\bullet}$) and superoxide ($O_2^{\bullet -}$) radicals; iii) the free radicals finally lead to the oxidation of the organic compounds.

Selective catalytic photo-oxidation of lignocellulose-based biomass are currently the subject of intensive research, since they can afford a wide range of valuable chemicals, including some sugar-derived platform compounds (e.g. succinic, 5,5-furandicarboxylic, 3-hydroxypropionic, gluconic, glucaric and levulinic acids and 3-hydroxybutyrolactone) [55]. The photocatalytic selective conversion of alcohols can be performed as well, but the reaction is highly dependent on the type of alcohol. The oxidation of primary alcohols is generally low, but high selectivities can be achieved (>95%). The initial step of the proposed mechanism is the interaction of a surface hole with the OH group of the alcohol, leading to metal-oxo species with proton removal. This proton removal step is easier for alcohols with increased carbon chain length and branching, and thus improved conversion can be achieved. Photocatalytic selective oxidation processes bring several benefits from energy and environmental viewpoints. More efforts should however be paid to the use of solar light irradiation in aqueous solution as a renewable source of energy for the heterogeneous selective photo-oxidation of a variety of biomass derivatives.

The combined use of sonochemistry (power ultrasound) and photocatalysis, called ***sonophotocatalysis***, recently found innovative applications in organic compounds reactions and biomass conversion (lignin, chitosan, etc.) to high-added value intermediates [56]. Under coupled UV/US irradiations, an increased amount of radical species is generated in the reaction medium ($HO^{\bullet}$, $O_2^{\bullet -}$, $HO_2^{\bullet}$) in the presence of a catalyst. Additionally, turbulence induced by the cavitation phenomenon (US irradiation) also increases, resulting in a simultaneous increase of catalytically active surface area through deagglomeration of the particles and hence on an enhanced mass transfer between the liquid phase and the catalyst surface. These beneficial effects account for an overall increased catalytic activity (Figure 3). Although the sonophotocatalytic technology is still in its infancy for the conversion of biomass and biomass-derived products to platform molecules, this is an avenue well worth exploring and special attention should be paid in the near future to its implementation.

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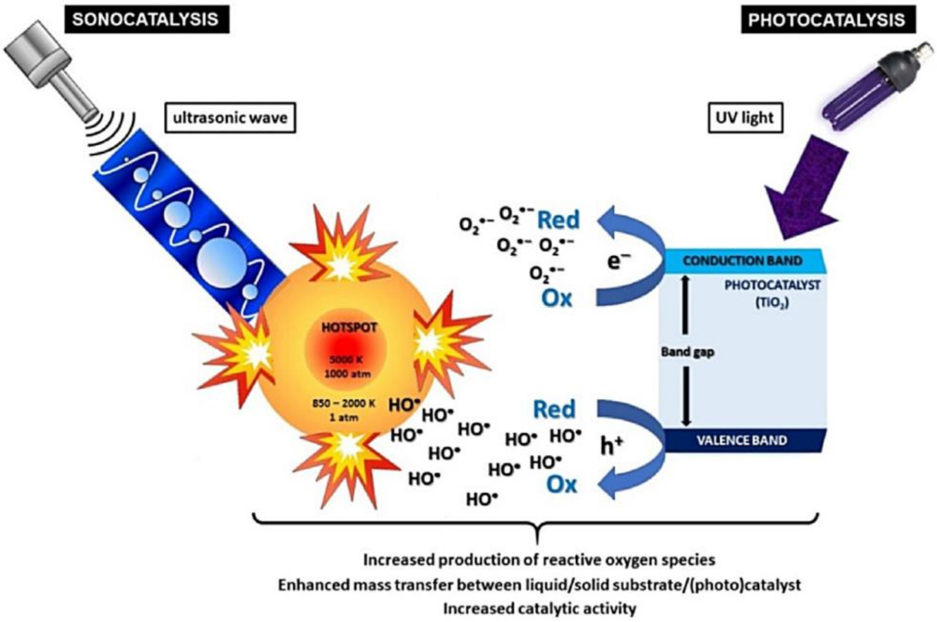

Figure 3. Schematic representation of the principle of sonophotocatalysis combining sonocatalysis and photocatalysis [56].

2.4. Unconventional Activation Methods for the Synthesis of Selective Oxidation Catalysts

In line with the use of unconventional activation methods for selective catalytic oxidation reactions, non-thermal activation techniques can also be appropriately used for the development of greener, cost-effective and generalized synthetic routes for designing catalytic materials with controlled characteristics and improved activity and selectivity. Ultrasound and microwave irradiations, ball milling and sonophotodeposition, to name a few strategies, represent innovative technologies to the conventional solid-state, wet chemistry and gas phase synthesis procedures. Many review articles can be found in the literature, offering a comprehensive discussion on the matter [57-61]. Here, through a few selected examples, we wish to highlight the advantages of using ultrasound, ball milling, sonophotodeposition and sonoelectrodeposition in the synthesis of solid catalysts (and photocatalysts) for the selective oxidation of alcohols to the corresponding aldehydes or carboxylic acids.

Ultrasound-assisted synthesis has been demonstrated to bring unexpected improvements in physical and physico-chemical properties of metal oxides, such as particle size and shape control, high purity phase, increased surface area, among others. Pure manganese octahedral molecular sieves (OMS-2) were synthesized by a direct sonochemical method at ambient temperature and pressure without any calcination step [62]. OMS-2 materials, exhibiting very high surface area (288 $m^2 g^{-1}$) and small particle sizes (1-7 nm), have been obtained, as compared to previously reported OMS-2 prepared under reflux conditions. The sonochemically synthesized materials also possess greater amounts of surface defects and have shown excellent catalytic activity in the selective oxidation of benzyl alcohol to benzyl aldehyde compared to conventionally prepared OMS-2 catalysts. Highly pure and crystalline 2D CuO nanoleaves have been synthesized at 25°C under low frequency ultrasound (19.95 kHz, 8.2 W electric power) and further used in the base-free aqueous oxidation of glycerol to dicarboxylic acids in the presence of hydrogen peroxide under mild reaction conditions [63]. The significant advantages of this ultrasonic route over conventional methods include a direct synthesis, incredibly fast experiments (5 min), non-thermal activation and in situ pseudo-calcination. Additionally, the CuO nanoleaves, prepared by the reported technique, have been observed to be more active, selective and robust (against leaching) than the corresponding nanoleaves prepared without ultrasound irradiation. Readers are also referred to the review of

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Domini et al. [49] for other examples of sonochemically-generated catalysts for various oxidation reactions.

Mechanochemically prepared catalysts can also display improved features over catalysts obtained through more traditional synthesis procedures, which are in many cases not environmentally friendly. The group of Luque has extensively used the one-step mechanochemical ball milling route to prepare advanced nanomaterials for catalysis and energy applications [59], such as supported metal and metal oxide nanoparticles, perovskites, nanocomposites, MOFs and bioconjugates (Figure 4). A series of mesoporous silica supported iron oxide nanoparticles were prepared by ball-milling and their catalytic properties were investigated in the selective oxidation of various alcohols with hydrogen peroxide [64]. Under optimum conditions (dry milling, 350 rpm, 10 min), the ball-milled catalysts consisting of low iron loaded Al-SBA-15 materials showed a higher catalytic activity in the microwave-assisted oxidation of benzyl alcohol to benzaldehyde with respect to Fe/Al-SBA-15 counterparts prepared by a conventional impregnation method.

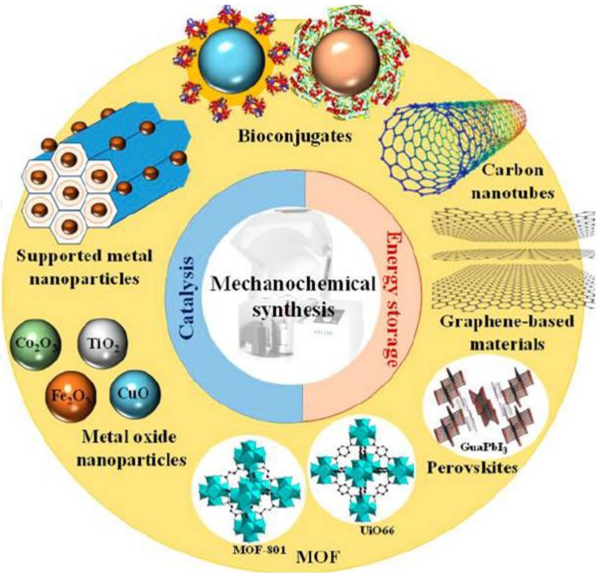

Figure 4. Schematic representation of advanced materials synthesized by a ball-milling route for catalytic and electrochemical energy storage applications [59].

Merging unconventional activation methods may also result in new powerful methodologies. In this sense, a variety of materials with controlled morphology and composition have been produced by the *in situ* coupling of ultrasound with chemical (electrochemical and photochemical) deposition methods. The mechanism of sonoelectro- and sonophotodeposition processes is different (electrochemical reactions vs. photoexcitation), but their synergism with sonication is essentially based on the cavitation phenomenon [61]. The resulting enhanced mass transfer is generally seen as the increase of electrochemical current (or current pulses) in the case of the sonoelectrodeposition process, thereby leading to deposits with enhanced mechanical properties and electrocatalytic properties. In the sonophotodeposition method, the cavitation process influences the transfer of photoexcited states which results in enhanced photochemical reaction rates and then in deposits with improved chemical properties (Figure 5).

Single-step sonoelectrodeposition of CdS nanoparticles with homogeneous distribution inside TiO_2 nanotubes (NTs) has been performed [65], leading to highly photoelectrochemically active materials (Ultrasonic bath, 40 kHz, 2.4 kW m^{-2}, constant current density of 5 mA cm^{-2}, 50°C). Most importantly, ultrasound did not damage the tubular structure of the nanotubes during the CdS sonoelectrodeposition process. The resulting CdS-TiO_2NTs electrodes produced a stronger photocurrent coupled to an extended photoresponse under visible light compared to the corresponding electrodes prepared by the electrodeposition method in silent conditions (without ultrasonic irradiation). To date only a few materials/catalysts have been prepared by the sonophotodeposition method that was implemented by the group of Colmenares [61]. For example,

Fe^{3+}-based nanoparticles (4-5 nm) were sonophotodeposited on a TiO_2/zeolite Y support material (Ultrasonic horn, 20 kHz, 700 W, 25% amplitude, sun-imitating Xenon lamp, 240-2000nm) [66]. The nanoparticles were found to be mainly located in the bulk of the photocatalyst due to the physical effect of ultrasound, with as a consequence better catalytic performances in the selective photo-oxidation of benzyl alcohol to benzaldehyde compared to the catalyst synthesized by an ultrasound-assisted wet impregnation procedure.

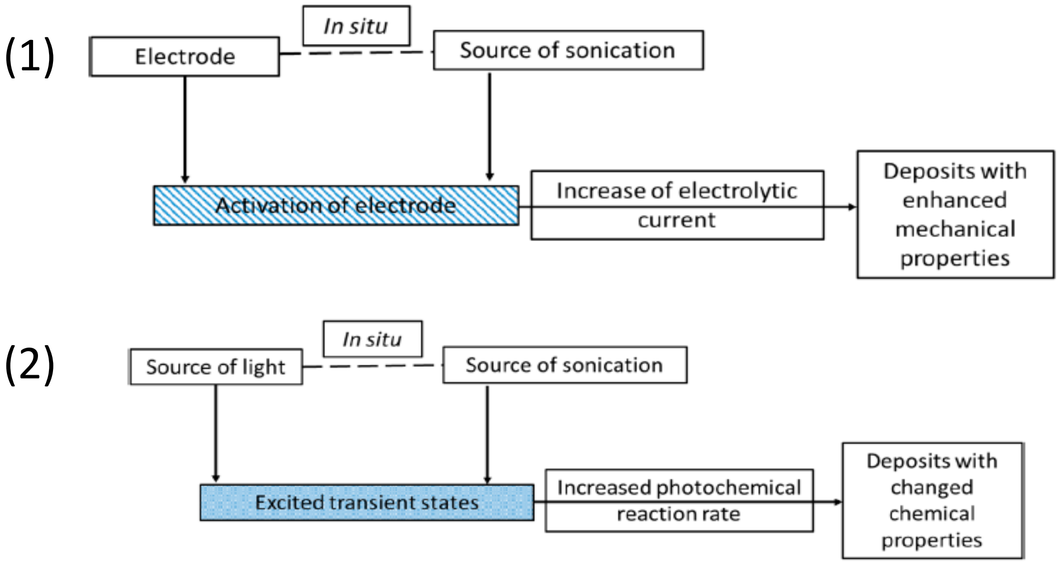

Figure 5. Schematic representation of the synthesis of materials by using the (1) sonoelectrodeposition and (2) sonophotodeposition processes, adapted from [61].

The few examples, given above, describe what can be done with the use of non-thermal activation methods in the synthesis of catalytic materials, exhibiting controlled features and improved efficiencies, and demonstrate that more researches are needed, since new activation procedures are able to improve catalytic properties.

3. Total Oxidation Reactions in Gas Phase and Liquid Phase

3.1. Gas Phase-Solid Catalyst Total Oxidation Reactions

This domain covers many reactions used for depollution treatments and combustion [67]. The main catalysts, used at present, are based on expensive noble metals, but many efforts have been carried out in the last two decades to replace them, in a number of processes, by much cheaper transition metal oxide-based catalysts (M = Ce, Co, Fe, Mn, Ni). For instance, perovskites ($LnBO_3$) in which Ln is a lanthanide (usually La) and B a cation which possesses two valence states as Co, Fe or Mn, e.g., $La_{1-x}M_xMnO_{3+\delta}$ with M = Ce or Sr, and also spinels, hexaaluminates and some other oxide structures have been proposed and studied. Hexaaluminates ($AB_xAl_{12-x}O_{19-\delta}$, where A and B are a lanthanide and a transition/noble metal cation, respectively), are formed of alternate layers of alumina spinel blocks and mirror planes in which a large A cation is located.

Single oxides have been shown to be active for total oxidation reactions (CO, methane, COVs, wet air oxidation …), as well as for the treatment of nitrogen, chlorinated and sulfided compounds, in particular NO_x, NH_3, urea. Their activity for total oxidation has been suggested to be due to $M^{n+}/M^{(n+1)+}$ ion pairs associated with oxygen vacancies, and subsequent adsorption or heterolytic splitting of the molecule (CO, hydrocarbons) and for O_2 activation. This is why oxides such as Co_3O_4 or Fe_3O_4, Mn- and Cu-based oxides are appropriate candidates for oxidation reactions [68], even in the absence of a noble metal. For instance, Cu- or Fe-exchanged zeolites have been used in DeNOx processes, because of their stability above 900°C.

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Volatile organic compounds (VOCs) are atmospheric pollutants, due to their high toxicity and malodorous nature, arising from mobile sources and industrial emissions. The degradation of VOCs has then become a major area of research in environmental protection during recent decades. Common VOCs, such as hydrocarbons, halogenated hydrocarbons, ketones, alcohols and aromatic compounds, are emitted in many industrial factories in their throwing away emissions. Traditional methods of removing VOCs from the polluted air stream include adsorption onto activated carbons or zeolites and thermal combustion. These processes have strong limitations due to the difficult recovery of the adsorbent after regeneration and low durability, due to the high temperature of VOC degradation. Many advanced technologies have been developed for the rapid and economical removal of VOCs from indoor air. Among the technologies proposed, catalytic oxidation appears as an innovative and promising approach, as the pollutants can be oxidized to H_2O and CO_2 and/or converted to relatively harmless compounds at low operating temperatures. Catalytic total oxidation is an effective technique for the treatment of industrial VOCs principally resulting from industrial processes using solvents, glue or insulating materials, and usually containing mono-aromatics particularly BTEX (benzene, toluene, ethylbenzene, xylenes) and oxygenated compounds (acetone, ethanol, butanone …). A series of catalysts have been evaluated for VOCs elimination. The most active catalysts particularly at low reaction temperatures (generally below 200°C or even at room temperature in some cases) turn out to be noble metals (Pd, Pt, Au, Ag) dispersed on high surface area transition metal oxide supports (γ-Al_2O_3, SiO_2, TiO_2, MnO_x, CeO_2 …) [69,70]. The mixture of such oxide supports was shown to increase the dispersion of noble metals while reducing their loading. However, the cost of catalysts is a main obstacle for the industrial application of these VOCs removal processes.

Compared with the expensive and scarce noble metals, single or mixed metal oxides are currently extensively studied as alternatives for the catalytic oxidation of VOCs at low temperature. The developed transition metal oxides are mainly based on p-type semi conductors multivalent metal oxides due to the highly mobile chemisorbed oxygen species, thereby leading to enhanced activity (Mn_3O_4, Mn_2O_3, MnO_2, Co_3O_4, CeO_2, $MnOx$-CeO_2, $MnOx$-ZrO_2, MnOx-CuO …) [71,72]. Additionally, for a same chemical composition, the catalytic performances of metal oxides are also governed by their structure/morphology owing to preferential exposure of different active sites, and hence to variable surface oxygen vacancy densities [73]. Transition metal oxides also have distinct advantages over noble metal-based catalysts in the removal of halogenated VOCs, since they exhibit a higher chlorine resistance. As a perfect illustration of the fact that metal oxides can now be considered as a good alternative to noble metals, a Co-Al-Ce mixed oxide (denoted as CoAlCeO), synthesized by the hydrotalcite route, was studied for the total oxidation of industrial VOCs (toluene, butanone and VOCs mixtures) and compared to palladium-based catalysts (Pd/α-Al_2O_3, Pd/H-FAU, Pd/CeO_2 and Pd/γAl_2O_3) [74]. Their catalytic performances were evaluated (taking into account the oxidation of by-products emitted from the process), highlighting the higher efficiency of the CoAlCeO mixed oxide than that of the Pd-based materials for the total oxidation of a VOCs mixture. Few studies have been carried out on the catalytic oxidation of VOCs mixtures, especially at low concentration, even though this is a crucial step for industrial VOCs removal applications. Inhibition phenomena and molecules adsorption competition have been generally observed [75], which makes it difficult to find appropriate and efficient catalysts. Moreover the oxidation mechanism of mixed VOCs is probably quite different from that of single VOC and more work should be done on these aspects. More efforts must also be devoted to the study of the reaction mechanisms of transition metal oxides by in situ characterization techniques, so as to develop highly active non-precious catalysts for VOCs oxidation.

In addition to catalytic oxidation, photocatalysis has also been investigated for the decomposition of VOCs and other organic compounds on single or mixed metal oxides, such as TiO_2, N-doped TiO_2 and highly donor-doped layered perovskites catalysts [76-78]. When illuminated with UV or visible light, photocatalysts can generate strong active species able to decompose VOCs at low temperature. Simple reaction equipment is required, but problems of low selectivity for many VOCs photocatalysts have been reported [79].

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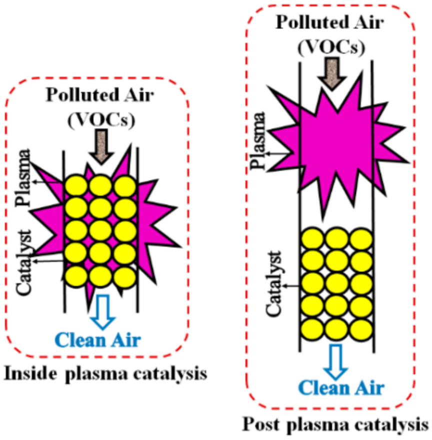
With the aim of improving the removal efficiency of industrial VOCs and/or highly diluted VOCs, hybrid treatments combining catalytic oxidation with other technologies (ozonation, non-thermal plasma …) are found to not only integrate the advantages of the individual technologies, but also are more effective to treat diverse and complex VOCs in the stream than do the single technology, while increasing the selectivity to CO_2 [79]. For instance, catalytic oxidation of a large variety of VOCs have been carried out with ozone at low temperatures (20-100°C) over noble metal-based catalysts and transition metal oxides. Currently, a large number of studies have been focused on unsupported or supported manganese oxides, since highly active oxygen species are formed by decomposition of O_3 on MnOx oxides which can further oxidize VOCs at low temperatures [80-82]. Catalytic ozonation has been proven to be an alternative method particularly suited for the removal of low concentration VOCs pollution present in factory/workshop, meeting room, etc. However, one of the most important considerations is that highly efficient catalysts must be developed so as to avoid any potential secondary pollution. Catalysts capable of converting low VOC concentration at ambient conditions with a rational use of ozone should be found, so that the simultaneous removal of both pollutants and ozone occurs with no residual O_3 at the end of the reaction.

The combination of ***non-thermal plasma*** (NTP) with catalysis has also attracted significant interest for VOCs decomposition, offering several advantages, namely energy efficiency, product selectivity and satisfactory carbon balance [83]. NTP consists of energetic electrons, ions, reactive radical species, neutral particles/molecules and UV photons (e^-, $O^\bullet$, $HO_2^\bullet$, $HO^\bullet$, $N_2^\bullet$, O_3, etc.). These species can decompose VOCs at ambient conditions, although the overall process is not selective to CO_2. Such drawback can be overcome by using hybrid plasma processes, such as the combination of NTP with catalysis. One of the key parameter when referring to non-thermal plasma catalytic oxidation is the location of the catalyst with respect to the plasma reactor that should be carefully considered to achieve a synergistic effect [84]. The catalyst can be integrated either inside the plasma reactor (IPC/ ***Inside Plasma Catalysis***) or downstream of the discharge region (PPC/ ***Post Plasma Catalysis***), as shown in Figure 6.



Inside plasma catalysis

Post plasma catalysis

Figure 6. Schematic representation of the IPC (Inside Plasma Catalysis) and PPC (Post Plasma Catalysis) configurations [85].

The reaction mechanism of a zeolite-plasma hybrid system for the decomposition of toluene at room temperature was studied using gas and surface FTIR analyses [86]. The authors have investigated different configurations of the zeolite hybrid reactor and have shown that the main factor, improving the reaction mechanism, was the ozone generated in the gas phase by the plasma which reacted with toluene adsorbed onto the zeolite. Non-thermal plasma can also combine with photocatalysis to build up efficient hybrid treatments.

As described in § 2.3, microwaves and ultrasound have been used as activation tools during the synthesis of transition metal oxides for VOCs degradation as well. For instance, it was reported that Co-Al hydrotalcite-like catalysts prepared by a microwave-assisted synthesis route were the

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most active in toluene oxidation than the corresponding oxides obtained by a traditional co-precipitation method, owing to a higher content of Co^{2+} species on the catalyst surface and hence to a greater amount of O_{II} species available for the reaction [87].

3.2. Liquid Phase-Solid Catalyst Total Oxidation Reactions

Wet air oxidation (WAO) is a process by which degradation of organic pollutants occurs in liquid-phase by oxidation with oxygen under pressure. WAO is employed to treat industrial waste waters at moderate temperatures (180–315°C) and at pressures from 2 to 15 MPa. However, lower energy requirements and significantly higher oxidation efficiencies can be achieved when adding homogeneous or heterogeneous catalysts. Such process is designated as catalytic wet air oxidation (CWAO). In addition to supported precious metal catalysts, oxide-based catalysts can also be used but care should be taken so as to avoid leaching of metallic ions. The treatment of toxic nitrogen-containing compounds, which are mainly produced in the chemical and pharmaceutical industries, is one of the major applications of a CWAO process. For instance, many studies have been done for the oxidation of aniline, which is often chosen as model molecule of a dye-industry pollutant. Particular attention has been paid to selectivity toward organic by-products (especially azo, nitroso and nitro compounds, phenolic compounds and carboxylic acids) and inorganic forms of nitrogen (NH_4^+, N_2, NO_2^-, NO_3^-). Ammonia is one of the most refractory by-products, which unfortunately is formed during catalytic WAO of nitrogen-containing organic pollutants and is itself a pollutant. However, high selectivities to dinitrogen have been obtained on certain noble metal-based catalysts. Multifunctional catalysts have also been proposed for the treatment of nitrogenous organic compounds. More information on catalytic wet air oxidation processes for the treatment of refractory organic pollutants and industrial wastewaters can be found in recent review papers [88-90].

When the oxidation is performed with hydrogen peroxide instead of oxygen, the process is designated as wet peroxide oxidation (WPO) and the corresponding catalytic oxidation process is referred to as CWPO. Ozone can also be used as oxidant in ozonation processes, while UV irradiation is exploited in photocatalysis.

Advanced oxidation processes (AOPs) are near ambient temperature and pressure water treatment processes based on the *in situ* generation of highly reactive hydroxyl radicals (HO•) able to oxidize recalcitrant organic pollutants to smaller intermediates or to complete mineralization to CO_2 and water. Formation of hydroxyl radicals can be achieved by using various oxidants (H_2O_2, O_3, UV) in chemical, sono-chemical, photo-chemical and electro-chemical processes and their combination [91]. Less conventional AOPs include ionizing radiation, non-thermal plasma and supercritical water oxidation. A schematic classification of advanced oxidation processes is presented in Figure 7. For example, photocatalysis may lead to the oxidation and the reduction of organic compound pollutants in water into intermediates containing oxygen, CO_2, H_2O and a mineral acid when a heteroatom such as nitrogen or chlorine is present. The photocatalytic reaction may be used in many domains such as the elimination of odor from drinking water, the degradation of oil spills in surface-water systems, or the degradation of harmful organic contaminants, such as herbicides, pesticides, and refractive dyes.

One of the most frequently used AOP is based on the Fenton process, where HO• radicals are generated during activation of H_2O_2 by metallic cations (i.e. Fe^{2+}). However, in order to overcome the major drawbacks of the homogeneous system (iron removal, sludge production, etc.), heterogeneous Fenton-type systems have been prepared to catalyze the oxidation of various organic pollutants in mild reaction conditions. A large variety of Fenton-like processes are available depending on the method used for the production of hydroxyl radicals, namely the photo-Fenton-like, electro-Fenton-like, sono-Fenton-like and microwave-Fenton-like processes, as well as their combined use, such as the photo-electro-Fenton-like, sono-photo-Fenton-like and sono-electro-Fenton-like, to name a few. The advances in the application of Fenton-like oxidation processes for the treatment of wastewater have been recently reviewed by several authors [91-93].

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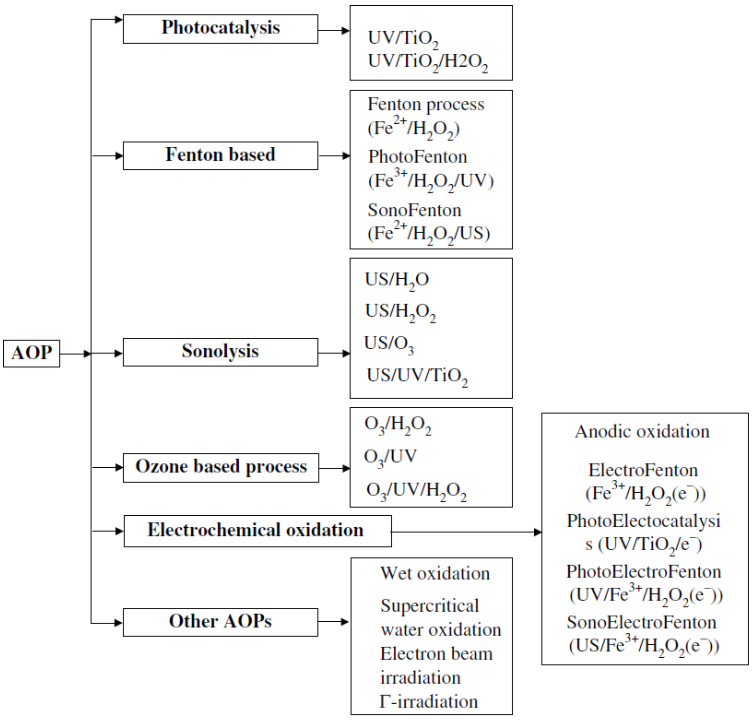

Figure 7. Classification of advanced oxidation processes [91].

The combination of sonocatalysis with photocatalysis has been widely investigated in the last fifteen years as AOP for the degradation of a large variety of organic pollutants in aqueous phase [56], such as phenolic compounds, dyes, pharmaceuticals, pesticides and textile industrial effluents [94]. The combined effects of such sonophotochemical process (see 2.3), coupled to the efficient use of a photocatalyst, result in an increased production of free radicals in aqueous solution and of cavitation bubbles, enhance mass transfer between the pollutants and the photocatalyst, as well as remove any impurities from its surface. Hence, an increase of the reaction rates of pollutants degradation is observed.

A novel method based on catalytic ozonation coupled to high-frequency ultrasound and Fe species was recently developed [95] for decomposing anti-inflammatory pharmaceutical ibuprofen (IBP) present in waste water. The pH value was found to be the most crucial parameter among the variables investigated in this sonocatalytic ozonation process (concentration of IBP, ozone flow rate, US power, pH, catalyst dosage …). It determined the mass transfer, diffusion of ozone and organic solutes from the bulk liquid to the gas-liquid/liquid-solid interfaces, formation of reactive oxygen species which promoted Fenton-like reactions, as well as the reactivity of the Fe species. The oxidation and mineralization degree of IBP were highly enhanced in 40 min of reaction under simultaneous US/O_3/Fe conditions compared to single ultrasound irradiation (US/Fe) and ozonation (O_3/Fe) processes.

In summary, many AOPs have been reported so far for the degradation of refractory compounds in liquid phase. Further investigations are however required to identify scale-up parameters including reactors design.

4. Conclusion

In this review we have provided several types of oxidation reactions (selective/partial or total, gas-solid and liquid-solid phases), of oxidation catalysts and of activation procedures, illustrated by case studies or industrial application, mainly gathered in the last two decades. It is well known that many oxidation reactions, particularly in selective oxidation domain, have been industrialized in the second part of the 20th century and beginning of this century for total oxidation. Gas solid oxidation reactions have been mainly studied and applied last century. However, with the increased environmental issues and legislation constraints, new processes or improved processes have been

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developed more recently. This is why depollution has been largely and widely studied in the past two or three decades and that liquid phase heterogeneous catalysis has been developed, particularly when biomass raw material products were available and wastewaters are to be more efficiently depolluted. We have also emphasized that selectivity is a major factor to look for in heterogeneous catalysis, which necessitate to control and avoid undesired by-products, particularly in industrial processes and in pharmaceutical and medical domains.

We have also shown that eco-compatible activation methods based on ultrasound and microwaves irradiations, grinding, electro and photo-activated processes offer challenging opportunities for the selective conversion of a library of alcohols and biomass-derived compounds, as well as for total oxidation reactions of pollutants both in gas phase and liquid phase. These non-thermal activation technologies often surpass the effects of conventional thermal conditions by increasing reaction rates, shortening reaction times, improving activity and selectivity, while being cost- and energy efficient. They represent a very challenging but quite promising domain for future researches for a more sustainable world.

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