



## Review

## Recent advances on wet air oxidation catalysts for treatment of industrial wastewaters



Francesco Arena<sup>a,b,\*</sup>, Roberto Di Chio<sup>a</sup>, Bianca Gumina<sup>b</sup>, Lorenzo Spadaro<sup>b</sup>, Giuseppe Trunfio<sup>a</sup>

<sup>a</sup> Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, Viale F. Stagno D'Alcontres 31, I-98166 Messina, Italy

<sup>b</sup> Institute CNR-ITAE "Nicola Giordano", Salita S. Lucia 5, I-98126 S. Lucia (Messina), Italy

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## ABSTRACT

The pressing need to prevent further damages to environment and deterioration of natural resources urges a global effort to shift from the current *money-making* industrial policies to a *sustainable development* pattern. This requires an easy availability of handy and economical technologies for depollution of gas and liquid wastes, "green" industrial manufacturing processes and "zero-emission" energy supply systems. In this context the purification and reuse of industrial wastewaters represents a very critical environmental issue because of the global freshwater shortage, the continuing water resources depletion, and the increasing pollutants release. In this context, the heterogeneous catalytic wet air oxidation (CWAO) is nowadays considered the most promising technology for large-scale application to detoxification of noxious wastewaters, provided that robust, effective and cost-effective catalysts are available. Then, this work provides an overview of mechanistic and kinetic issues of the homogeneous and heterogeneous CWAO of several classes of industrial pollutants, at basis of recent advances on design and development of supported noble metal and oxide catalysts.

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## 1. Introduction

Since more than two decades the issue of wastewater detoxification has become a topic of major concern, pressed by a constantly increasing world population and the consequent growth of agricultural and industrial activities, currently accounting for more than 90% of global freshwater consumption [1]. This implies

continuous resources depletion and pollutants emission, while *ca.* 1 billion people globally lack access to safe water supplies and *ca.* 2.6 billion are without access to basic sanitation, particularly in the least developed regions of Asia, Central and South America, and Africa [1]. Considering that the lack of clean-water accessibility causes almost one-tenth of diseases worldwide, the improvement of the quality of drinking water and the reduction of water contamination are very challenging issues, worthy of a global business exceeding \$93 billion in 2016 [2].

Among the existing technologies nowadays available for wastewater purification, the conventional biological treatment is the most used, despite it requires large volumes and long residence

\* Corresponding author at: Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, Italy. Tel.: +39 0906765606; fax: +39 090391518.

E-mail address: [Francesco.Arena@unime.it](mailto:Francesco.Arena@unime.it) (F. Arena).

times and is not feasible for wastewaters containing microbial-growth inhibiting compounds. Alternative processes like Adsorption, Advanced Oxidation (AOP), and Incineration are suitable only for small-scale applications because of high costs and complexity [3–7], whereas the heterogeneous catalytic wet air oxidation (CWAO) offers high versatility and efficiency in the abatement of various classes of industrial pollutants and remarkable economy-scale advantages [7–11]. Then, a big scientific and technological concern is devoted worldwide at discovering robust, cheap, and efficient solid catalysts, ensuring the mineralization (i.e., total oxidation) of toxic and recalcitrant polluting compounds to water, carbon dioxide and nitrogen, at mild reaction conditions [5–7,9].

Despite preliminary treatments, like heavy metals precipitation, to avoid poisoning phenomena, stability and lifetime of CWAO catalysts are affected by the severe operating conditions, due to the strong oxidizing aqueous reaction medium, often acidic, containing complex mixtures of inorganic and organic substances, which cause *poisoning*, *sintering*, *fouling*, *overoxidation*, and *leaching* phenomena [7–9,12,13]. In particular, the active phase leaching remains the most remarkable drawback of metal oxide catalysts [12,14–18] that, besides causing deactivation and secondary pollution problems, enables a *homogeneous* reaction path, often disguising the reactivity pattern of solid catalysts [19–23]. Hence, current CWAO catalyst formulations mostly include either noble-metals like Pt, Pd, and Ru [6,7,9,12,13], or  $\text{MnO}_x$  species, as the active phase [6–9,12,13,24–31], in combination with oxide promoters, the most common of which is ceria [3,6–8,12]. As catalyst carrier, ceria ensures a high chemical resistance under CWAO conditions also promoting the total oxidation functionality because of its enhanced redox behavior, well-known as the “oxygen storage capacity” (OSC).

Apart from such basic features, the latest advances in catalyst development rely on recent mechanistic studies of several model compounds like phenol, carboxylic acids, and ammonia which highlighted the pathway of heterogeneous CWAO processes and some basic relationships among structure, activity, selectivity and stability for both noble-metal and metal oxide catalysts [24,27,28,30,31].

Therefore, this work is aimed at providing an overview of the reactivity pattern of homogeneous and heterogeneous CWAO catalysts and the relative mechanistic clues at basis of recent advances on catalysts development.

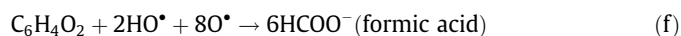
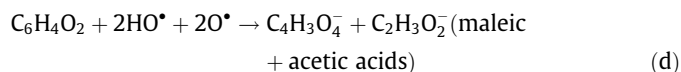
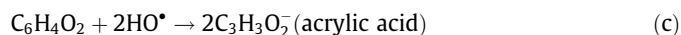
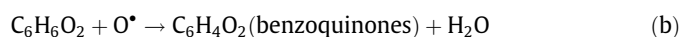
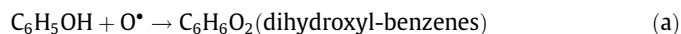
## 2. Homogeneous “free-radical” or heterogeneous “surface” L–H path?

An accurate knowledge of the reaction mechanism of catalytic reactions represents a fundamental step in the way of catalyst optimization and process development [7–10,13]. However, multi-phase nature of the CWAO process and various physical and chemical phenomena, affecting at once activity, selectivity, and stability of solid catalysts, render this goal particularly difficult [12]. In fact, a comprehensive understanding of the reaction paths implies a systematic characterization of the overall reaction system, including: (i) the *liquid phase*, to get information on substrate-TOC conversion, selectivity and metal leaching; (ii) the *gas phase*, to probe the formation of gaseous species (i.e.,  $\text{CO}_2$ , VOC's); and (iii) the *solid phase*, to monitor state and modifications of the catalytic system during and after the CWAO process [25,27,31–37]. Indeed, uncontrolled metal leaching phenomena, often promoting parallel homogeneous reaction paths, the lack of systematic studies on mechanism and kinetics, coupled to a routine detection of C1–C2 acidic intermediates, were taken as evidences of an unchanging *free-radical autocatalytic* path, driven by either homogeneous or heterogeneous CWAO catalysts [4–

8,14,15,20,21,23,25–27,38,39]. This led to speculate that solid catalysts enhance the efficiency of radical formation, according to a surface-assisted homogeneous path [4,8,20,21,23,27,28,38,39], whilst recent studies stress the key role of surface adsorption on the working mechanism of heterogeneous catalysts [13,22,23,25–28,30,32,33,40,41] that reflects in a reactivity pattern markedly different from that observed in homogeneous CWAO processes [31,42].

### 2.1. Homogeneous catalysis

The main mechanistic clues of the homogeneous *autocatalytic free-radical path* are evident from the wet air oxidation data of phenol in absence of catalyst (Fig. 1). These consist of an initial very low rate of phenol conversion followed by a faster kinetic regime, and a considerably lower extent of TOC abatement (Fig. 1A), accompanied by an extensive formation of numerous intermediates (Fig. 1B), confirming the occurrence of a poorly efficient and unselective radical reaction network [4,6–8,14,15,43]. In fact, a slow rate of conversion matches the initial production of oxygen-radicals driving the primary oxidation of phenol to catechol and hydroquinone (*initiation step*) that are further oxidized to benzoquinones; in turn, the high intrinsic reactivity of benzoquinones [4,8,44–47] speeds up the radical-chain propagation favoring the unselective rupture of the aromatic ring with the consequent formation of refractory C1–C4 intermediate species (*propagation step*), accounting for the final slow kinetic regime of the *termination step*:



A poor mineralization efficiency of the non-catalytic homogeneous radical path is evident from a huge formation of C1–C4 carboxylic acids, despite also the formation of heavy polymeric species is evident from the final brownish color of the reacting solution [48].

Although homogeneous  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  catalysts (5 ppm) markedly improve the rate of the CWAO process, typical “S-shaped” phenol conversion curves (Fig. 2), and the formation of many reaction intermediates (Table 1) confirm all the essential features of the *free-radical autocatalytic* pathway. In particular,  $\text{Cu}^{2+}$  is the most effective catalyst prompting a full phenol conversion in ca. 2 h after a very short induction time, while  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  catalysts drive a complete conversion of the substrate in 4 and 6 h respectively, after an induction time comparable to that of the blank test. Despite a final production of acetic acid comparable to that of the other catalysts [4,6–8,13,44,45,47,49], the superior efficiency of  $\text{Cu}^{2+}$  is also evident from higher  $\text{CO}_2$  selectivity at expense of C3–C4 intermediates (Table 1) [4–8]. In fact, the different catalytic behavior of Fe, Mn and Cu ions has been explained by different redox potentials controlling the rate of the catalyst-substrate-oxygen electron transfer-exchange process [43,44,47,50].

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