Inorganica Chimica Acta 431 (2015) 101–109

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Review

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

Francesco Arena [a,b,*], Roberto Di Chio [a], Bianca Gumina [b], Lorenzo Spadaro [b], Giuseppe Trunfio [a]

[a] Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, Viale F. Stagno D'Alcontres 31, I-98166 Messina, Italy
[b] Institute CNR-ITAE "Nicola Giordano", Salita S. Lucia 5, I-98126 S. Lucia (Messina), Italy

ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form 22 December 2014
Accepted 23 December 2014
Available online 17 January 2015

Keywords:
Wastewater treatment
Wet air oxidation
Homogeneous and heterogeneous catalysis
Organic pollutants
Transition metals
Reaction mechanism

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.

Contents

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 (F. Arena).

http://dx.doi.org/10.1016/j.ica.2014.12.017
0020-1693/

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 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., 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*:

$$C_6H_5OH + O^\bullet \rightarrow C_6H_6O_2(\text{dihydroxyl-benzenes}) \quad (a)$$

$$C_6H_6O_2 + O^\bullet \rightarrow C_6H_4O_2(\text{benzoquinones}) + H_2O \quad (b)$$

$$C_6H_4O_2 + 2HO^\bullet \rightarrow 2C_3H_3O_2^-(\text{acrylic acid}) \quad (c)$$

$$C_6H_4O_2 + 2HO^\bullet + 2O^\bullet \rightarrow C_4H_3O_4^- + C_2H_3O_2^-(\text{maleic} + \text{acetic acids}) \quad (d)$$

$$C_6H_4O_2 + 6O^\bullet \rightarrow C_4H_3O_4^- + C_2O_4H^-(\text{maleic} + \text{oxalic acids}) \quad (e)$$

$$C_6H_4O_2 + 2HO^\bullet + 8O^\bullet \rightarrow 6HCOO^-(\text{formic acid}) \quad (f)$$

$$C_6H_4O_2 + 12O^\bullet \rightarrow 6CO_2 + 2H_2O \quad (g)$$

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 Fe^{3+}, Mn^{2+} and 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, Cu^{2+} is the most effective catalyst prompting a full phenol conversion in *ca.* 2 h after a very short induction time, while Fe^{3+} and 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 Cu^{2+} is also evident from higher 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].

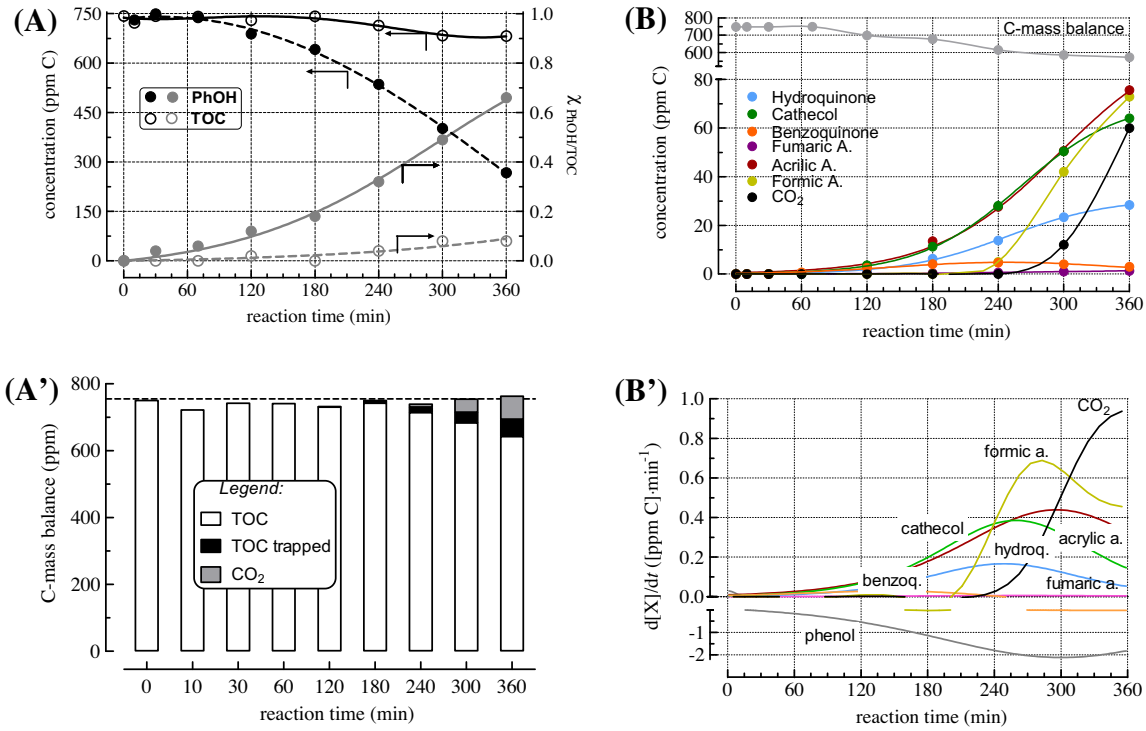


Fig. 1. Wet air oxidation (blank test) data of phenol at 150 °C. (A) concentration and conversion of phenol and TOC; A′) C-mass balance; (B) concentration of reaction intermediates and B′) formation rate of the various intermediates (Adapted from Ref. [31]. Copyright 2010 with permission from Elsevier).

2.2. Heterogeneous catalysts

Since the nineties Cu-based catalysts have been the topic of numerous investigations because of a remarkable performance in the CWAO of various model compounds [9,14–17]; nevertheless, metal leaching was immediately recognized as a major drawback for catalyst stability and secondary pollution phenomena [12]. Attempts to improve the chemical resistance of heterogeneous Cu catalysts were substantially unsuccessful [16,20,21,51,52], while the influence of leaching on their CWAO pattern was for longtime undervalued [14,15]. By contrast, systematic studies on the physico-chemical properties and dissolution rate of various copper supported systems revealed a close relationship between activity and extent of leaching [14,15], which is evident from the activity data of a co-precipitated $CuCeO_x$ catalyst in the range of 130–170 °C (Fig. 3). A temperature increase causes a considerable shortening of the induction time and an acceleration of phenol conversion with the consequent formation of acidic intermediates accounting for a marked decrease of pH [4,8,14,17,20,21,53–58]; in turn the acidic pH favors a progressive dissolution of the active phase that further accelerates phenol and TOC conversion. These trends are fixed by some peculiar relationships among pH, leaching and conversion, shown in Fig. 4. In particular, Fig. 4A documents the crucial effect of pH on the dissolution of Cu ions that, in turn, speed up the conversion rate of phenol and TOC *via* a parallel homogeneous free-radical path (Fig. 4B) [14,15,53,56].

Efforts to counteract Cu leaching by the enhancement of the metal-support interaction strength were not particularly encouraging [12,18], while the insulation of Cu particles by a thin PTFE hydrophobic film improves the resistance to leaching, but it strongly depresses the CWAO performance of a Cu/Al_2O_3 catalyst [51,52]. Alternatively neutral or alkaline-buffered solutions prevent an extensive dissolution of the active phase, even if this reflects in a remarkable activity decrease and the formation of more refractory and/or toxic reaction intermediates [14–17,47,53,55].

Likewise, Fe-based catalysts feature a CWAO pattern strongly influenced by the leaching of the active phase [12,44,59]; in fact, supported iron systems are mostly used in combination with hydrogen peroxide at low temperature in the attempt of immobilizing the Fe cations for AOP (i.e., Fenton) processes [44,59–62].

The above drawbacks are ultimately overcome by noble-metal or MnO_x-based systems, representing to date the most promising classes of heterogeneous CWAO catalysts. In particular, hindering any contribution of dissolved metal ions, the lack of significant leaching phenomena reflects in a catalytic pattern, diagnostic of a quite different reaction mechanism [12].

The reactivity pattern of a typical $MnCeO_x$ catalyst (Mn/Ce, 1) in the CWAO of phenol (Fig. 5) shows, in fact, the following peculiar features: (i) the lack of any *induction time* irrespective of temperature (110–150 °C); (ii) analogous *substrate and TOC conversion trends*, and (iii) *very fast reaction kinetics*, leading to a complete purification of the reacting solution in a very short time (10–20 min). An immediate CO_2 release indicates the lack of induction time also for the mineralization process, although its rate increases markedly with temperature, resulting in final CO_2 selectivity values rising from 20% (110 °C) to 85% (150 °C), respectively. Then, the heterogeneous CWAO proceeds via a very "clean" reaction path, although CO_2 selectivity values systematically lower than TOC conversion (Fig. 5) signals a gap in C-mass balance [27–29], which is explained by the TGA-DSC characterization data of the used catalyst samples (Fig. 6). Significant weight losses are associated to proportional exothermic signals in the range of 150–300 °C, denoting the occurrence of a combustion process of adsorbed C-containing species, to an extent bridging the X_{TOC}-S_{CO2} gap at different temperature (Fig. 6A) and time (Fig. 6B). Proving that the TOC abatement is not a measure of the mineralization efficiency of heterogeneous CWAO catalysts, the inverse relationship between weight loss and CO_2 selectivity indicates that the reactivity pattern of the $MnCeO_x$ catalyst mirrors a fast adsorption of the substrate leading to a simultaneous abatement of TOC, while a much slower oxidation rate of the adsorbed species leading to

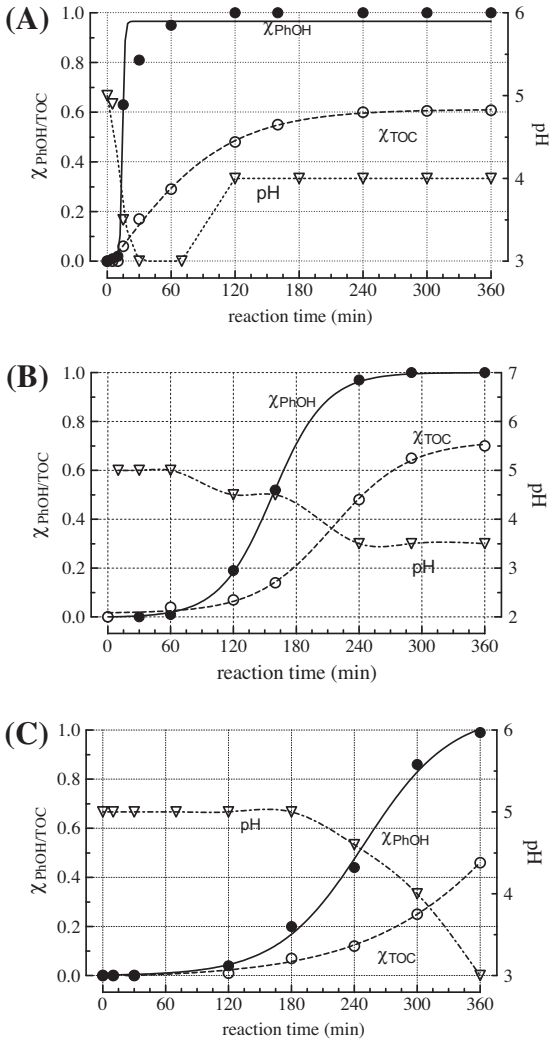


Fig. 2. Homogeneous CWAO of phenol at 150 °C with Cu^{2+} (A) Fe^{3+} (B) and Mn^{2+} (C) catalysts (5 ppm). Phenol and TOC conversion and pH vs. reaction time (Adapted from Ref. [31] Copyright 2010 with permission from Elsevier).

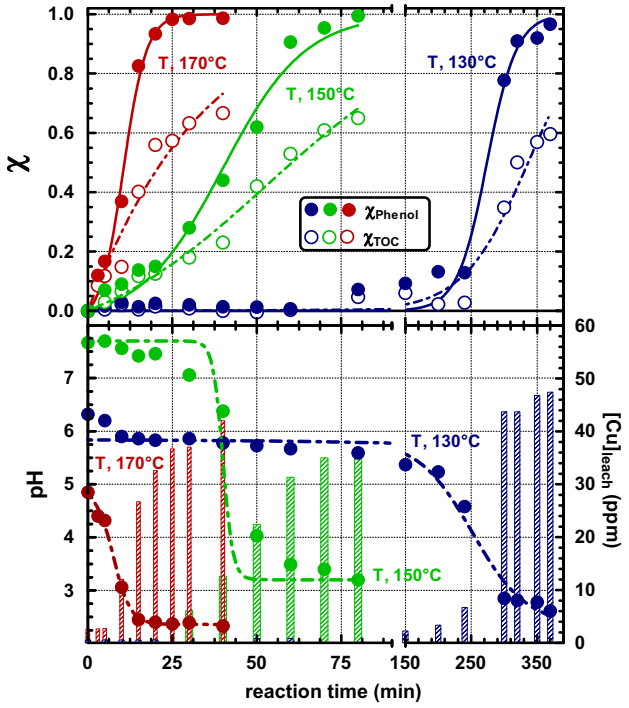


Fig. 3. Effect of the reaction temperature on the CWAO of phenol on $CuCeO_x$ catalyst (P_{O2}, 7 atm; R, 1). Phenol and TOC conversion vs. reaction time (*top panel*) and pH and $[Cu]_{leach}$ vs. reaction time (*bottom panel*) (Reprinted from Ref. [15]. Copyright 2006 with permission from Springer).

CO_2 (*mineralization*) and minor amounts of C1–C2 acids (*partial oxidation*) is likely the *rate limiting step* (*r.l.s.*) of the heterogeneous CWAO process [25,27,28,32,37].

A typical noble-metal catalyst (5% Pt/CeO_2) features a similar reactivity pattern in the CWAO of phenol, although a worse performance is evident from slower conversion and mineralization rates, mostly at lower catalyst-to-substrate ratios (Table 2) [42].

These evidences are consistent with a typical surface Langmuir–Hinshelwood reaction mechanism (Scheme 1) that, besides accounting for a very "clean" activity pattern, explains the strong tendency of heterogeneous systems to undergo deactivation by C-species (i.e., fouling) generated by side surface reaction(s) [23–28,34–36,42].

The remarkable differences of the homogeneous and heterogeneous CWAO processes are definitively fixed by the activity–selectivity relationships shown in Fig. 7; in fact, the parallel growth of substrate and TOC conversion mirrors the selective character of the surface adsorption, while exponential trends stress the unselective behavior of homogeneous systems and the promoting role of reaction intermediates on the propagation step of the *autocatalytic free-radical* path [30,46].

3. CWAO of various model compounds

Although toxicity and presence in a large number of wastewater streams press a major concern on phenol and its derivatives, carboxylic acids, and N-compounds are also main targets of the CWAO process, since the former are residual intermediates of degradation of heavier organic pollutants [14–17,46,47,53,54,63,64], while the

Table 1
Product selectivity at different conversion level in the homogeneous CWAO of phenol (T, 150 °C) (*Adapted from Ref.* [31]. *Copyright 2010 with permission from Elsevier*).

Catalyst	Conv.	Selectivity (%)										
		C6			C4		C3		C2		C1	
		hyq.	cath.	bzq.	mln. a.	fum. a.	mal. a.	acr. a.	ox. a.	ac. a.	for. a.	CO_2
Fe^{3+}	0.2	7	15	14	0	0	0	16	0	0	47	0
	0.5	8	15	4	7	0	0	18	0	10	31	7
	1.0	0	0	0	9	0	0	1	1	48	6	37
Mn^{2+}	0.2	10	5	23	0	1	0	62	0	0	0	0
	0.5	12	26	8	0	1	0	37	0	0	0	16
	1.0	0	1	0	0	0	0	12	2	47	11	27
Cu^{2+}	0.5	7	11	7	0	0	0	21	1	46	8	0
	1.0	0	0	0	0	0	0	0	1	48	2	49

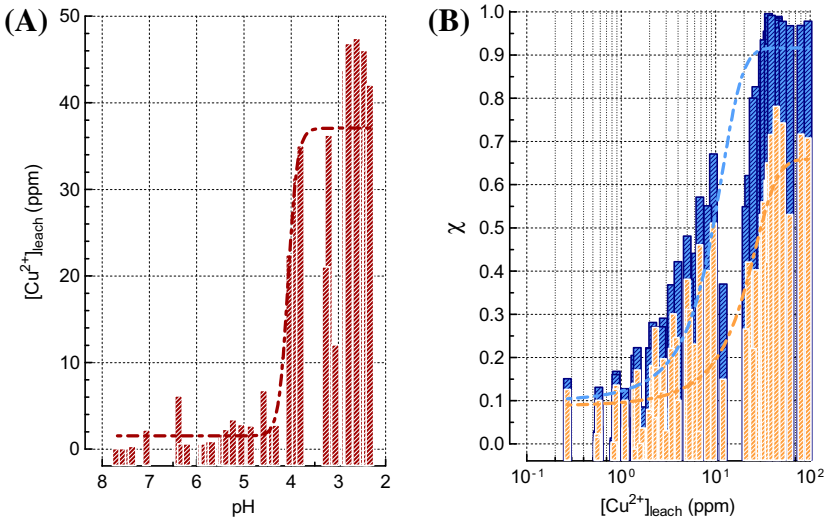


Fig. 4. Summary of CWAO activity data of the $CuCeO_x$ catalyst: $[Cu]_{leach}$ vs. pH (left panel) and phenol and TOC conversion vs. $[Cu]_{leach}$ (right panel) (Reprinted from Ref. [15]. Copyright 2006 with permission from Springer).

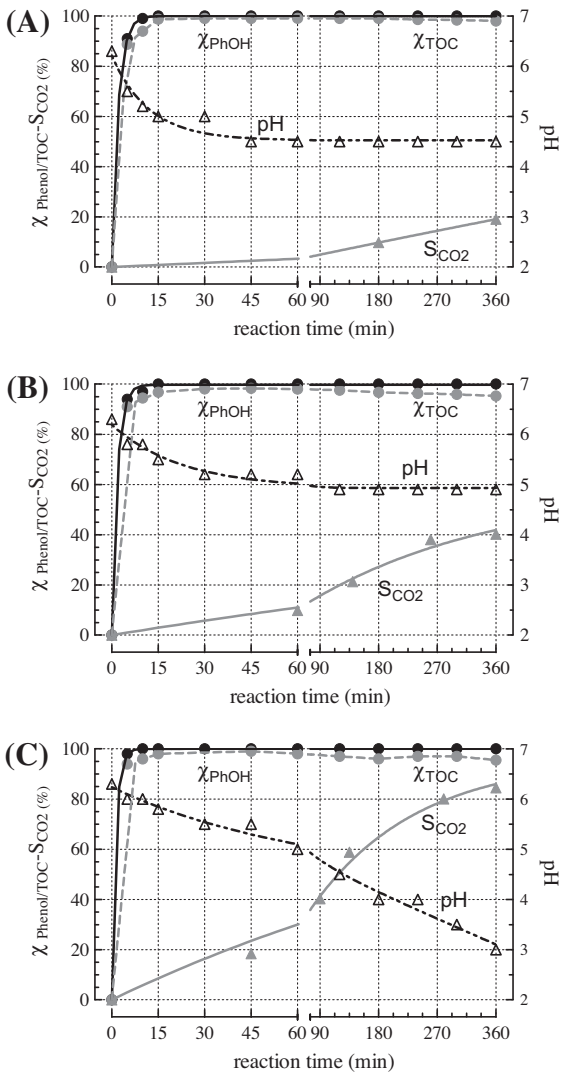


Fig. 5. CWAO pattern of phenol (catalyst-to-phenol weight ratio of 5) of the $MnCeO_x$ catalyst at 110 (A), 130 (B) and 150 °C (C) (Reprinted from Ref. [36]. Copyright 2014 with permission from Elsevier).

mineralization of N-compounds requires very active and selective catalysts, avoiding the formation of very toxic intermediates [63–72].

Then, Silva et al. carried out an exploratory investigation of the reactivity of several ceria-supported oxide catalysts in the CWAO of acrylic acid, finding out that at 200 °C the Mn/Ce system attains a 98% TOC conversion (2 h), higher than both MnO_x (95%) and Ag/Ce (85%) catalysts, respectively [73]. Although all Ce-promoted catalysts showed faster reaction rates than bare MnO_x system, they indicated an optimum Mn/Ce ratio (70/30) ensuring a better performance in the CWAO process [73].

Arena et al. recently used a "model" $MnCeO_x$ catalyst (Mn/Ce, 1) obtained by the redox-precipitation route [74], showing that is effective in the CWAO of formic and acetic acids (T, 110–150 °C; catalyst-to-substrate weight ratio, 5) [36]. Despite the same L–H reaction mechanism, lower conversion rates than phenol were ascribed to the different adsorption mechanism of carboxylic acids. In particular, electrostatic interactions of carboxylate species with positively charged hydroxyls of the catalyst surface explain the promoting effect of the acidic strength of the substrate on the relative adsorption rate (e.g., conversion) and the poor reactivity of the corresponding salts [36].

Several studies also addressed the reactivity of noble-metal catalysts in the CWAO of carboxylic acids at lower catalyst-to-substrate weight ratios, but, under harder conditions [40,41,75–81]. Studying the CWAO of stearic acid (T, 160–230 °C; P_{O2}, 2 MPa) on ceria supported Pt, Ir, Ru and Pd (5%) catalysts, Renard et al. found a higher reactivity for the Pt/CeO_2 system, while Ru/CeO_2 showed a performance comparable to the bare ceria support [81]. Although the adsorption of large amounts of C-species on the catalysts surface, the Pt/CeO_2 system ensured their progressive mineralization with a minor release of acetic acid [81].

Comparing the reactivity of (5%) Pt and Ru supported on CeO_2, $ZrCeO_2$ and $ZrCePrO_2$, Mikulová et al. found that the Pt/CeO_2 system also exhibits a better performance in the CWAO of acetic acid (T, 200 °C), despite ruthenium features much higher (280–2530 h^{-1}) turnover frequencies (TOF) than Pt catalyst (49–94 h^{-1}). Due to the lack of correlation between catalytic activity and OSC, they also stressed that the latter leads to an extensive formation of surface carbonate species, responsible of a drastic drop in activity [40,41]. Despite similar catalyst formulation, the same authors reported a significantly lower mineralization activity of acetic acid under analogous reaction conditions (*ca.* 30%) for a

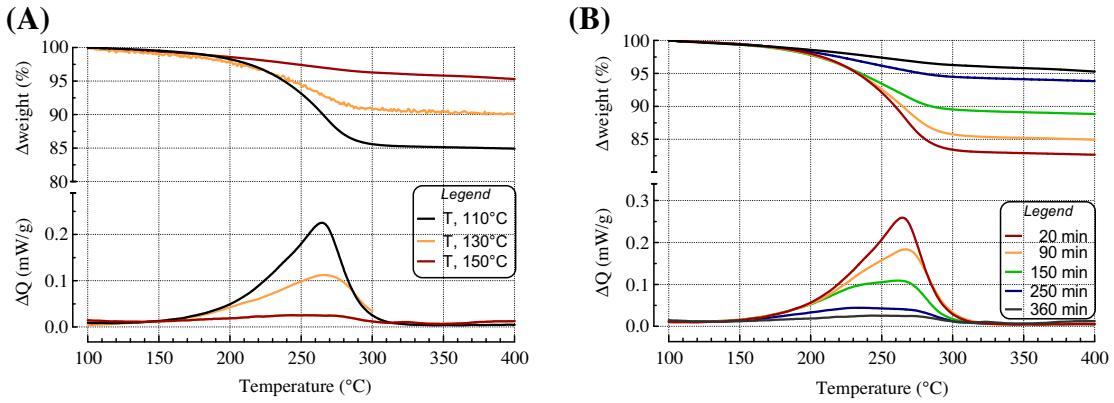
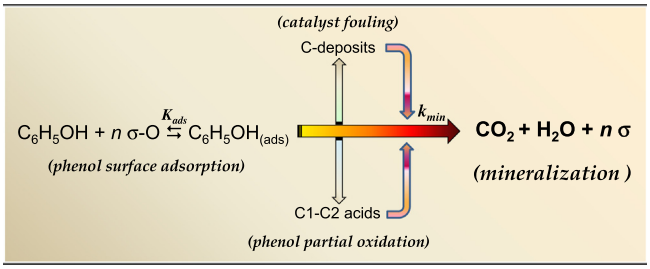


Fig. 6. TGA-DSC data of the used $MnCeO_x$ catalyst samples in the CWAO of phenol at different temperature (110–150 °C) after 6 h of reaction time (A) and at 150 °C after different reaction time (B) (Reprinted from Ref. [36]. Copyright 2014 with permission from Elsevier).

Table 2
Final (6 h) phenol and total organic carbon (TOC) conversion, CO_2 selectivity, theoretic carbon content and weight loss (TGA) data of the used catalyst samples (*adapted from Ref.* [42]. *Copyright 2012 with permission from Elsevier*).

Catalyst	*R*	$X_{Ph,fin}$ (%)	$X_{TOC,fin}$ (%)	$S_{CO2,fin}$ (%)	Δ_{CMB}[a](%)	VOC (%)	C-content[b] (%)	ΔW_{TGA}[c](%)
Pt/CeO_2	5	100	95	50	−45	–	−8	−6
	1	40	30	10	−20	13	−7	−6
$MnCeO_x$	5	100	85	60	−25	–	−5	−5
	1	100	80	20	−60	–	−38	−40

[a] Difference between $X_{TOC,fin}$ and S_{CO2}.
[b] Theoretic carbon content of the used catalysts.
[c] Weight loss of the used catalysts recorded by TGA analysis.



Scheme 1. Simplified reaction scheme of the heterogeneous CWAO of phenol.

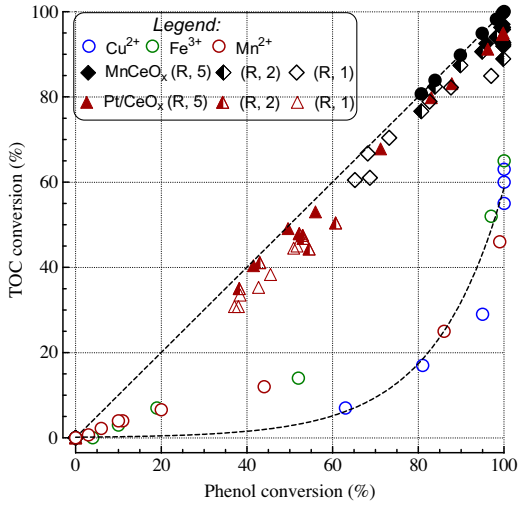


Fig. 7. Summary of TOC vs. phenol conversion data of the homogeneous and heterogeneous CWAO processes (Adapted from Ref. [42]. Copyright 2012 with permission from Elsevier).

low surface area (2.5%) Pt/CeO_2 catalyst, indicating an optimum Pt crystallite size, ensuring higher TOF (200–250 h^{-1}) and catalyst stability for a metal dispersion in the range of 5–25% [40]. Further investigation documented a negligible influence of support composition on the reactivity of Ru and a higher intrinsic activity as the metal particle size increases [82]. By contrast, studying the influence of the support composition (i.e., CeO_2, TiO_2 and ZrO_2 and their combination) on the reactivity of Ru catalysts in the CWAO of acetic acid (T, 200 °C; P, 4 MPa), Wang et al. reported a reactivity scale matching the surface concentration of non-lattice oxygen (*defect oxide*) [83].

Ammonia represents another major environmental threat because of a high toxicity and presence in wastewater of large industrial manufacture plants (fertilizers, urea, metallurgy, etc.), also forming during the degradation of organic N-containing compounds [84,85]. A preliminary study on the reactivity of ceria-supported noble metal catalysts (e.g., Pt, Pd, Ru and bi-metallic systems) in the CWAO of ammonia and aniline (T, 150–250 °C; P_{O2}, 2 MPa) showed that at T ⩾ 200 °C a Ru/CeO_2 catalyst achieves a complete degradation of aniline, with a selectivity to nitrogen of *ca.* 50%; at higher temperature the conversion rate is extremely high, but larger amounts of nitrite and nitrate are produced [84]. Hence, combining the high activity of Ru with the high N_2 selectivity of Pd in the CWAO of ammonia, a bimetallic $PdRu/CeO_2$ catalyst and an optimum temperature of 200 °C have been pointed as the best compromise to attain a complete conversion of aniline with a 90% N_2 selectivity [84].

Carbon Sibunit supported Pt, Pd and Ru catalysts are also very active in the CWAO of phenol and aniline at 160 °C but, despite a total conversion of both substrates, a complete mineralization was attained with 0.4–0.6%Ru + 5%CeO_2/Sibunit catalyst formulation [66].

A systematic comparison of the reactivity of noble metal catalysts in the CWAO of nitrogen and oxygen containing pollutants

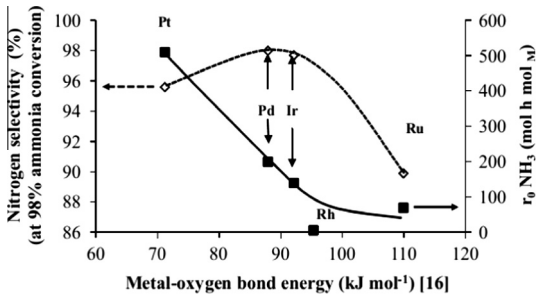


Fig. 8. Initial oxidation rate of ammonia and N_2 selectivity vs. the metal–oxygen bond energy. (Reprinted from Ref. [63]. Copyright 2014 with permission from Elsevier).

was carried out by Barbier et al., showing that high surface area Ru/CeO_2 catalyst attains a complete aniline conversion in 1 h at 200–230 °C [67]. Beside to a partial conversion of the substrate, the formation of condensed oligomers, like azobenzene, azoxybenzene or hydrazobenzene, is responsible of a progressive catalyst deactivation by formation of carbonaceous deposits at low temperature (160–200 °C). Similar reactivity scales in the CWAO of phenol and acetic acid, which are the most abundant intermediates of the oxidative degradation of aniline, were also recorded, while a higher N_2 selectivity of the Pd/CeO_2 catalyst in the CWAO of ammonia lead to argue that the association of Ru and Pd in bimetallic catalysts should be more effective for the mineralization of mixtures of oxygen and nitrogen containing pollutants [84].

Basic insights into the activity–selectivity pattern of noble metal catalysts in the CWAO of ammonia are provided by a recent study of Lousteau et al. [63]. Namely, comparing the rate of ammonia conversion and product formation (Fig. 8), they argued that the metal–oxygen bond energy plays a key-role on activity and selectivity [63]; the oxidation activity decreases as the metal–oxygen bond energy increases, while a volcano-shaped curve for nitrogen selectivity signals that the surface oxygen coverage should not be too high to promote the N–N recombination. In particular, ammonia is initially converted into nitrites and, then, part of nitrites is oxidized to nitrates, while another part is reduced to molecular nitrogen via retro-disproportionation reaction between ammonium and nitrites ions [63,85]. Lee et al. explained the preferential formation of N_2 by a homogeneous reaction between NO_2^- and NH_4^+ ions as, even under highly oxidizing conditions, nitrite ions are more likely to form molecular nitrogen rather than be oxidized to nitrates [85].

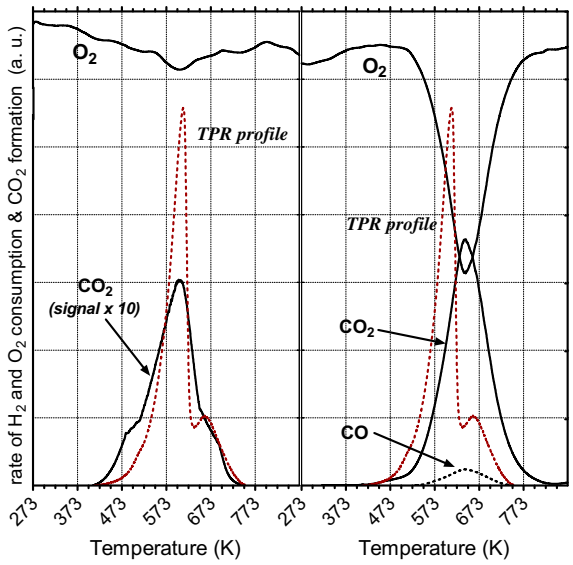


Fig. 9. TPR pattern of a co-precipitated $MnCeO_x$ catalyst and TPO profiles of phenol deposited on a "fresh" catalyst sample (left panel) and of a "used" sample (right panel) (Reprinted from Ref. [37]. Copyright 2007 with permission from American Chemical Society).

4. Catalyst optimization

Despite a superior purification efficiency enabled by a surface L–H reaction path, a slow oxidation rate of the adsorbed species, beside to the continuous formation of CO_2, accounts for an incipient release of partial oxidation products (i.e., C1–C2 acids) and the surface accumulation of C-containing species, constituting the main weakness affecting selectivity and stability of noble metal and manganese oxide catalysts, respectively [3,23,25–27,29,86–90]. In turn, this indicates that phenol mineralization, partial oxidation products (release), and C-species accumulation occur via a consecutive-parallel reaction network (Scheme 1); the relative rate of these processes determines the selectivity-stability pattern, being controlled by the oxidation strength of the catalyst, as indicated by the direct relationship between reducibility and phenol oxidation activity in Fig. 9 [37].

The above mechanistic findings uncover that *chemical stability*, *textural properties* and *redox activity* are basic requirements to build robust and efficient CWAO catalysts [37,74], as documented by a short survey of recent advances on catalyst design and development [91–94].

Despite systematic studies on the CWAO of phenol by co-precipitated MnO_x–CeO_2 catalysts showed that a composite Mn/Ce (70/30) oxide exhibits a better performance than 1% Pt/Al_2O_3 catalyst in the range of 80–130 °C [23], the mineralization activity was the major drawback, also causing the formation of deactivating carbonaceous deposits [22,23,25,26,30]. In order to improve the total oxidation functionality, hindering at once the formation of C-deposits, Larachi et al. scrutinized the effects of Pt and/or Ag addition, finding a better mineralization selectivity and maintenance of higher activity (110 °C) because of marked improvement of catalyst reducibility [22]. Later, the same research group claimed that K-doping enhances to much higher extent the resistance to fouling of the $MnCeO_x$ catalyst (Mn_{at}/Ce_{at}, 1/1) [25,26], although its reduction behavior was similar to non-promoted catalyst [26]. Abecassis-Wolfovich et al. reported similar results for a co-precipitated $MnCeO_x$ catalyst in terms of phenol adsorption capacity and deactivation pattern (80–130 °C), stressing a minor influence of K, Cs, Pt, and Ru promoters thereon [27]. However, arguing the potential for catalyst improvement by increasing the *amount of metal and oxygen ions at the surface, bulk density, surface area, interface, and redox ability*, they devised a *nanocasting* strategy to improve the efficiency of $MnCeO_x$ catalysts. Using silica scaffolds they prepared *nanocasted* catalysts, consisting of crystalline nanodomains (d, 2–3 nm) of Mn_2O_3 and CeO_2 phases, with surface area up to 300 m^2/g [29,70,94]. Despite a conversion rate of 2,4,6,-trichlorophenol (120 °C) similar to a reference co-precipitated system, it attained a TOC conversion of 94% in comparison to a 14% value of the latter one [29]. The same catalyst is efficient in the CWAO of aniline (100–140 °C), although a relevant Mn leaching due to the complexation ability of the substrate, which is suppressed by acidification of the reacting solution [70].

Likewise, Alarco and Talbot exploited the *confinement effect* using carbon black as scaffold and an anionic surfactant to attain *nanosized* $MnCeO_x$ composites active in the detoxification of Bayer liquors [93], whereas *nanostructured* $MnCeO_x$ catalysts were also obtained by a simple synthesis route involving redox reactions (*redox-precipitation*) between $KMnO_4$ and Ce(III)-Mn(II) precursors.

$$\begin{cases} MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 \Downarrow + 4HO^- & (1) \\ Mn^{2+} + 4HO^- \rightarrow MnO_2 \Downarrow + 2e^- + 2H_2O & (2) \\ Ce^{3+} + 4HO^- \rightarrow CeO_2 \Downarrow + e^- + 2H_2O & (3) \end{cases}$$

The simultaneous generation of the oxide phases favors the formation of MnO_x and CeO_2 nanodomains aggregating into homogeneously sized ($d \approx 20$ nm) oxide clusters, with a fully amorphous architecture resistant to the subsequent calcination treatment [35,74,87,91,95]. Large surface area and active phase exposure, along with a remarkable surface Mn-enrichment in a wide composition range were recognized as basic features accounting for the enhanced reducibility and mineralization activity of redox-precipitated catalysts [31,35,37,74,87,91,95]. These show a high performance also in the CWAO of p-cumaric acid and oil-mill wastewater in terms of activity, selectivity and stability [80].

5. Concluding remarks

A great scientific effort is in place worldwide for developing novel and cost-effective wastewater detoxification technologies.

The catalytic wet air oxidation (CWAO) appears nowadays as the most promising technology for developing rational water-policies based on the effective recycle-reuse of industrial process waters and decontamination of wastewaters.

Mechanistic evidences of the CWAO of several model compounds indicate in high *chemical stability*, *surface exposure* and *redox activity* the main requirements of heterogeneous CWAO catalysts.

Whatever the nature of the active phase (i.e., noble metal or metal oxide), CWAO catalyst formulations include ceria as structural and/or electronic promoter.

Ceria-promoted noble metal (i.e., Pt, Pd, Ru) and manganese oxide catalysts ensure the best performance in the CWAO of various model pollutants at $T < 250$ °C in terms of activity, selectivity and stability against leaching phenomena.

Efficiency and operating conditions of the CWAO process depend on the nature and reactivity of the substrate, although the "cross-effects" of different polluting species deserve adequate optimization of catalyst formulation and proper reactor engineering for the detoxification of "real" industrial wastewaters.

References

[1] UNICEF and World Health Organization, Progress on Drinking-Water and Sanitation: 2012 Update, 2012.
[2] J. Wilson, Water and Wastewater Treatment Technologies: Global Markets, Report code ENV008B, 2012.
[3] S. Imamura, in: A. Trovarelli, (Ed.), Catalysis by Ceria and Related Materials, Imperial College Press, London, UK, 14 (2002), p. 431.
[4] Y.I. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (1998) 309, http://dx.doi.org/10.1021/ie9702439.
[5] F. Luck, Catal. Today 53 (1999) 81, http://dx.doi.org/10.1016/S0920-5861(99)00112-1.
[6] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, J. Hazard. Mater. 160 (2008) 265, http://dx.doi.org/10.1016/j.jhazmat.2008.03.045.
[7] S.K. Bhargava, J. Tardio, J. Prasad, K. Fo, D.B. Akolekar, S.C. Grocott, Ind. Eng. Chem. Res. 45 (2006) 1221.
[8] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743, http://dx.doi.org/10.1021/ie980576l.
[9] K.-H. Kim, S.-K. Ihm, J. Hazard. Mater. 186 (2011) 16, http://dx.doi.org/10.1016/j.jhazmat.2010.11.011.
[10] A. Cybulski, Ind. Eng. Chem. Res. 46 (2007) 4007, http://dx.doi.org/10.1021/ie060906z.
[11] J. Hertrampf, A.H. Shadiakhy, Chem. Eng. (1997).
[12] S. Keav, J. Barbier Jr., D. Duprez, Catal. Sci. Technol. 1 (2011) 342, http://dx.doi.org/10.1039/c0cy00085j.
[13] F. Larachi, Top. Catal. 33 (2005) 109, http://dx.doi.org/10.1007/s11244-005-2518-0.
[14] F. Arena, R. Giovenco, T. Torre, A. Venuto, A. Parmaliana, Appl. Catal. B Environ. 45 (2003) 51, http://dx.doi.org/10.1016/S0926-3373(03)00163-2.
[15] F. Arena, E. Alongi, P. Famulari, A. Parmaliana, G. Trunfio, Catal. Lett. 107 (2006) 39, http://dx.doi.org/10.1007/s10562-005-9729-7.
[16] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. Garcia-Ochoa, Appl. Catal. B Environ. 61 (2005) 323, http://dx.doi.org/10.1016/j.apcatb.2005.06.006.
[17] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, Chem. Eng. Sci. 60 (2005) 4866, http://dx.doi.org/10.1016/j.ces.2005.04.015.
[18] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A Gen. 212 (2001) 175, http://dx.doi.org/10.1016/S0926-860X(00)00855-3.
[19] A. Pintar, J. Levec, J. Catal. 135 (1992) 345, http://dx.doi.org/10.1016/0021-9517(92)90038-J.
[20] S. Hočevar, J. Batista, J. Levec, J. Catal. 184 (1999) 39, http://dx.doi.org/10.1006/jcat.1999.2422.
[21] S. Hočevar, U.O. Krašovec, B. Orel, A.S. Aricó, H. Kim, Appl. Catal. B Environ. 28 (2000) 113, http://dx.doi.org/10.1016/S0926-3373(00)00167-3.
[22] S. Hamoudi, A. Sayari, K. Belkacemi, L. Bonneviot, F. Larachi, Catal. Today 62 (2000) 379.
[23] S. Hamoudi, F. Larachi, A. Sayari, J. Catal. 177 (1998) 247, http://dx.doi.org/10.1006/jcat.1998.2125.
[24] F. Arena, Catal. Sci. Technol. 4 (2014) 1890, http://dx.doi.org/10.1039/c4cy00022f.
[25] S.T. Hussain, A. Sayari, F. Larachi, J. Catal. 201 (2001) 153, http://dx.doi.org/10.1006/jcat.2001.3233.
[26] S.T. Hussain, A. Sayari, F. Larachi, Appl. Catal. B Environ. 34 (2001) 1, http://dx.doi.org/10.1016/S0926-3373(01)00204-1.
[27] M. Abecassis-Wolfovich, M.V. Landau, A. Brenner, M. Herskowitz, Ind. Eng. Chem. Res. 43 (2004) 5089, http://dx.doi.org/10.1021/ie049756n.
[28] M. Abecassis-Wolfovich, R. Jothiramalingam, M.V. Landau, M. Herskowitz, B. Viswanathan, T.K. Varadarajan, Appl. Catal. B Environ. 59 (2005) 91, http://dx.doi.org/10.1016/j.apcatb.2005.01.001.
[29] M. Abecassis-Wolfovich, M. Landau, A. Brenner, M. Herskowitz, J. Catal. 247 (2007) 201, http://dx.doi.org/10.1016/j.jcat.2007.01.015.
[30] H. Chen, A. Sayari, A. Adnot, F. Larachi, Appl. Catal. B Environ. 32 (2001) 195, http://dx.doi.org/10.1016/S0926-3373(01)00136-9.
[31] F. Arena, C. Italiano, A. Raneri, C. Saja, Appl. Catal. B Environ. 99 (2010) 321, http://dx.doi.org/10.1016/j.apcatb.2010.06.039.
[32] F. Larachi, I. Iliuta, K. Belkacemi, Catal. Today 64 (2001) 309, http://dx.doi.org/10.1016/S0920-5861(00)00534-4.
[33] F. Larachi, K. Belkacemi, S. Hamoudi, A. Sayari, Catal. Today 64 (2001) 163, http://dx.doi.org/10.1016/S0920-5861(00)00521-6.
[34] S. Keav, A. Martin, J. Barbier Jr., D. Duprez, Catal. Today 151 (2010) 143, http://dx.doi.org/10.1016/j.cattod.2010.01.025.
[35] F. Arena, G. Trunfio, J. Negro, L. Spadaro, Appl. Catal. B Environ. 85 (2008) 40, http://dx.doi.org/10.1016/j.apcatb.2008.06.020.
[36] F. Arena, C. Italiano, G. Drago Ferrante, G. Trunfio, L. Spadaro, Appl. Catal. B Environ. 144 (2014) 292–299, http://dx.doi.org/10.1016/j.apcatb.2013.07.025.
[37] F. Arena, J. Negro, A. Parmaliana, L. Spadaro, G. Trunfio, Ind. Eng. Chem. Res. 46 (2007) 6724, http://dx.doi.org/10.1021/ie0701118.
[38] A. Eftaxias, PhD thesis, Universitat Rovira i Virgili, Tarragona, Spain, 2002.
[39] A. Pintar, Appl. Catal. B Environ. 47 (2004) 143, http://dx.doi.org/10.1016/j.apcatb.2003.08.005.
[40] J. Mikulová, J. Barbier Jr., S. Rossignol, D. Mesnard, D. Duprez, C. Kappenstein, J. Catal. 251 (2007) 172, http://dx.doi.org/10.1016/j.jcat.2007.07.008.
[41] J. Mikulová, S. Rossignol, J. Barbier Jr., D. Mesnard, C. Kappenstein, D. Duprez, Appl. Catal. B Environ. 72 (2007) 1, http://dx.doi.org/10.1016/j.apcatb.2006.10.002.
[42] F. Arena, C. Italiano, L. Spadaro, Appl. Catal. B Environ. 115–116 (2012) 336, http://dx.doi.org/10.1016/j.apcatb.2011.12.035.
[43] J. Vicente, R. Rosal, M. Díaz, Ind. Eng. Chem. Res. 41 (2002) 46, http://dx.doi.org/10.1021/ie010130w.
[44] A. Quintanilla, J. Casas, A. Mohedano, J. Rodriguez, Appl. Catal. B Environ. 67 (2006) 206, http://dx.doi.org/10.1016/j.apcatb.2006.05.003.
[45] H.R. Devlin, I.J. Harris, Ind. Eng. Chem. Fundam. 23 (1984) 387, http://dx.doi.org/10.1021/i100016a002.
[46] D. Duprez, F. Delanoë, J. Barbier Jr., P. Isnard, G. Blanchard, Catal. Today 29 (1996) 317, http://dx.doi.org/10.1016/0920-5861(95)00298-7.
[47] A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, Top. Catal. 33 (2005) 181, http://dx.doi.org/10.1007/s11244-005-2524-2.
[48] A. Quintanilla, N. Menéndez, J. Tornero, J.A. Casas, J.J. Rodríguez, Appl. Catal. B Environ. 81 (2008) 105, http://dx.doi.org/10.1016/j.apcatb.2007.11.034.
[49] K. Pirkanniemi, M. Sillanpää, Chemosphere. 48 (2002) 1047. http://www.ncbi.nlm.nih.gov/pubmed/12227510.
[50] I.M. Kolthoff, E.B. Sandell, E.J. Mehan, S. Bruckenstein, Quantitative Analytical Chemistry, vol. 1, Piccin Edition, Padua, Italy, 1973.
[51] R.J. Fenoglio, P.A. Massa, F.D. Ivorra, P.M. Haure, J. Chem. Technol. Biotechnol. 82 (2007) 481, http://dx.doi.org/10.1002/jctb.1694.
[52] P. Massa, F. Ivorra, P. Haure, R. Fenoglio, Catal. Commun. 10 (2009) 1706, http://dx.doi.org/10.1016/j.catcom.2009.05.014.
[53] A. Santos, E. Barroso, F. García-Ochoa, Catal. Today 48 (1999) 109.
[54] A. Santos, P. Yustos, A. Quintanilla, S. Rodríguez, F. García-Ochoa, Appl. Catal. B Environ. 39 (2002) 97, http://dx.doi.org/10.1016/S0926-3373(02)00087-5.
[55] A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, Appl. Catal. B Environ. 53 (2004) 181, http://dx.doi.org/10.1016/j.apcatb.2004.04.022.
[56] A. Pintar, J. Levec, Chem. Eng. Sci. 47 (1992) 2395, http://dx.doi.org/10.1016/0009-2509(92)87066-Y.
[57] A. Pintar, J. Levec, Ind. Eng. Chem. Res. 33 (1994) 3070, http://dx.doi.org/10.1021/ie00036a023.
[58] J. Levec, A. Pintar, Catal. Today 24 (1995) 51, http://dx.doi.org/10.1016/0920-5861(95)00006-2.

[59] A. Quintanilla, J. Casas, J. Zazo, A. Mohedano, J. Rodriguez, Appl. Catal. B Environ. 62 (2006) 115, http://dx.doi.org/10.1016/j.apcatb.2005.07.001.
[60] A. Quintanilla, M.T. Kreutzer, J.A. Casas, F. Kapteijn, J.J. Rodriguez, J.A. Moulijn, Int. J. Chem. React. Eng. 5 (2007). Article A62.
[61] A. Quintanilla, J.A. Casas, J.J. Rodríguez, Appl. Catal. B Environ. 76 (2007) 135, http://dx.doi.org/10.1016/j.apcatb.2007.05.019.
[62] E. Guélou, J. Barrault, J. Fournier, J.-M. Tatibouët, Appl. Catal. B Environ. 44 (2003) 1, http://dx.doi.org/10.1016/S0926-3373(03)00003-1.
[63] C. Lousteau, M. Besson, C. Descorme, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.03.043.
[64] L. Oliviero, J. Barbier Jr., D. Duprez, Appl. Catal. B Environ. 40 (2003) 163.
[65] S. Morales-Torres, A.M.T. Silva, A.F. Pérez-Cadenas, J.L. Faria, F.J. Maldonado-Hódar, J.L. Figueiredo, et al., Appl. Catal. B Environ. 100 (2010) 310, http://dx.doi.org/10.1016/j.apcatb.2010.08.007.
[66] N.M. Dobrynkin, M.V. Batygina, A.S. Noskov, P.G. Tsyrulnikov, D.A. Shlyapin, V.V. Schegolev, et al., Top. Catal. 33 (2005) 69, http://dx.doi.org/10.1007/s11244-005-2507-3.
[67] J. Barbier Jr., L. Oliviero, B. Renard, D. Duprez, Top. Catal. 33 (2005) 77, http://dx.doi.org/10.1007/s11244-005-2509-1.
[68] S. Keav, A.E. de los Monteros, J. Barbier, D. Duprez, Appl. Catal. B Environ. 150–151 (2014) 402, http://dx.doi.org/10.1016/j.apcatb.2013.12.028.
[69] G. Ersöz, S. Atalay, Ind. Eng. Chem. Res. 50 (2011) 310, http://dx.doi.org/10.1021/ie1016706.
[70] R. Levi, M. Milman, M.V. Landau, A. Brenner, M. Herskowitz, Environ. Sci. Technol. 42 (2008) 5165, http://dx.doi.org/10.1021/es703070h.
[71] E. Gulin, Ind. Eng. Chem. Res. 49 (2010) 1625.
[72] J. Garcia, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Catal. Today 102–103 (2005) 101, http://dx.doi.org/10.1016/j.cattod.2005.02.013.
[73] A.M.T. Silva, R.R.N. Marques, R.M. Quinta-Ferreira, Appl. Catal. B Environ. 47 (2004) 269, http://dx.doi.org/10.1016/j.apcatb.2003.09.019.
[74] F. Arena, G. Trunfio, J. Negro, B. Fazio, L. Spadaro, Chem. Mater. 19 (2007) 2269, http://dx.doi.org/10.1021/cm070198n.
[75] D.-K. Lee, D.-S. Kim, Catal. Today 63 (2000) 249, http://dx.doi.org/10.1016/S0920-5861(00)00466-1.
[76] J. Bèziat, M. Besson, P. Gallezot, S. Durécu, J. Catal. 182 (1999) 129, http://dx.doi.org/10.1006/jcat.1998.2352.
[77] D.P. Minh, P. Gallezot, M. Besson, Appl. Catal. B Environ. 63 (2006) 68, http://dx.doi.org/10.1016/j.apcatb.2005.09.009.
[78] D.P. Minh, P. Gallezot, S. Azabou, S. Sayadi, M. Besson, Appl. Catal. B Environ. 84 (2008) 749, http://dx.doi.org/10.1016/j.apcatb.2008.06.013.
[79] D.P. Minh, P. Gallezot, M. Besson, Appl. Catal. B Environ. 75 (2007) 71, http://dx.doi.org/10.1016/j.apcatb.2007.03.015.
[80] F. Arena, D. Lombardo, G. Drago Ferrante, C. Italiano, L. Spadaro, G. Trunfio, Desalin. Water Treat. (2013) 1, http://dxdoi.org/10.1080/19443994.2013.867412.
[81] B. Renard, J. Barbier Jr., D. Duprez, S. Durécu, Appl. Catal. B Environ. 55 (2005) 1, http://dx.doi.org/10.1016/j.apcatb.2004.06.017.
[82] J. Gaálová, J. Barbier Jr., S. Rossignol, J. Hazard. Mater. 181 (2010) 633, http://dx.doi.org/10.1016/j.jhazmat.2010.05.059.
[83] J. Wang, W. Zhu, X. He, S. Yang, Catal. Commun. 9 (2008) 2163, http://dx.doi.org/10.1016/j.catcom.2008.04.019.
[84] J. Barbier Jr., L. Oliviero, B. Renard, D. Duprez, Catal. Today 75 (2002) 29, http://dx.doi.org/10.1016/S0920-5861(02)00040-8.
[85] D.K. Lee, J.S. Cho, W.L. Yoon, Chemosphere 61 (2005) 573, http://dx.doi.org/10.1016/j.chemosphere.2005.03.011.
[86] A.F.J. Santiago, J.F. Sousa, R.C. Guedes, C.E.M. Jerônimo, M. Benachour, J. Hazard. Mater. 138 (2006) 325, http://dx.doi.org/10.1016/j.jhazmat.2006.05.118.
[87] F. Arena, G. Trunfio, J. Negro, L. Spadaro, Mater. Res. Bull. 43 (2008) 539, http://dx.doi.org/10.1016/j.materresbull.2007.05.007.
[88] L.-X. Yang, Y.-J. Zhu, G.-F. Cheng, Mater. Res. Bull. 42 (2007) 159, http://dx.doi.org/10.1016/j.materresbull.2006.04.038.
[89] G. Xia, W. Tong, E.N. Tolentino, N. Duan, S.L. Brock, J. Wang, et al., Chem. Mater. 13 (2001) 1585.
[90] F. Arena, T. Torre, C. Raimondo, A. Parmaliana, Phys. Chem. Chem. Phys. 3 (2001) 1911, http://dx.doi.org/10.1039/b100091h.
[91] F. Arena, L. Spadaro, S.P.A. Nico, Nano-structured composite materials based on compositions of manganese and cerium, usable as oxidation catalysts and/or molecular adsorbers, WO 2012168957 A1, 2012. <https://www.google.com/patents/WO2012168957A1?cl=en&dq=WO+2012168957&hl=it&sa=X&ei=NmI4VO6wOuH4yQPTp4KIBg&ved=0CB8Q6AEwAA> (accessed 10.10.14).
[92] N. Okada, Y. Nakanishi, Y. Harada, Oxidation with a supported metal catalyst, US 4141428, 1977. <https://www.google.com/patents/US4141828?dq=4141828&hl=it&sa=X&ei=UEj_U7iUBsO-0QWqt4DABg&ved=0CB0Q6AEwAA> (accessed 28.08.14).
[93] P.C.T. J.A. Alarco, Removing organic impurities from Bayer process liquors, WO 2010105305 A1, 2010. <https://www.google.com/patents/WO2010105305A1?cl=en&dq=WO+2010105305&hl=it&sa=X&ei=PmE4VL-CAeHNygO8_oGQBg&ved=0CB8Q6AEwAA> (accessed 10.10.14).
[94] M. Landau, M. Herskowitz, M. Abecassis-Wolfovich, Manganese oxide-cerium oxide composite, WO 2007069238 A1, 2007. <http://www.google.com/patents/WO2007069238A1?cl=en&hl=it> (accessed 10.10.14).
[95] F. Arena, G. Trunfio, B. Fazio, J. Negro, L. Spadaro, J. Phys. Chem. C 113 (2009) 2822, http://dx.doi.org/10.1021/jp8068249.