



## Invited review

# Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review

Kyoung-Hun Kim, Son-Ki Ihm\*

Department of Chemical and Biomolecular Engineering (BK21 program), KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

## ARTICLE INFO

### Article history:

Received 30 July 2010

Received in revised form 27 October 2010

Accepted 4 November 2010

Available online 11 November 2010

### Keywords:

Catalytic wet air oxidation (CWAO)

Advanced oxidation process (AOP)

Heterogeneous catalyst

Industrial wastewater

Wastewater treatment

## ABSTRACT

Catalytic wet air oxidation (CWAO) is one of the most economical and environmental-friendly advanced oxidation process. It makes a promising technology for the treatment of refractory organic pollutants in industrial wastewaters. Various heterogeneous catalysts including noble metals and metal oxides have been extensively studied to enhance the efficiency of CWAO. The present review is concerned about the literatures published in this regard. Phenolics, carboxylic acids, and nitrogen-containing compounds were taken as model pollutants in most cases, and noble metals such as Ru, Rh, Pd, Ir, and Pt as well as oxides of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ce were applied as heterogeneous catalysts. Reports on their characterization and catalytic performances for the CWAO of aqueous pollutants are reviewed. Discussions are also made on the reaction mechanisms and kinetics proposed for heterogeneous CWAO and also on the typical catalyst deactivations in heterogeneous CWAO, i.e. carbonaceous deposits and metal leaching.

© 2010 Elsevier B.V. All rights reserved.

## Contents

1. Introduction	17
2. Heterogeneous catalytic wet air oxidation	17
2.1. Catalytic wet air oxidation of phenolic compounds	17
2.1.1. Catalytic wet air oxidation of phenol	17
2.1.2. Catalytic wet air oxidation of substituted phenol	20
2.2. Catalytic wet air oxidation of carboxylic acids	21
2.3. Catalytic wet air oxidation of N-containing compounds	22
2.3.1. Catalytic wet air oxidation of aniline	22
2.3.2. Catalytic wet air oxidation of dyes	23
2.3.3. Catalytic wet air oxidation of ammonia	23
2.4. Catalytic wet air oxidation of industrial wastewaters	24
2.5. Integration of catalytic wet air oxidation to other processes	25
3. Reaction mechanisms and kinetics for catalytic wet air oxidation	26
3.1. Reaction mechanisms and pathways	26
3.2. Reaction kinetics	27
4. Catalyst deactivation in catalytic wet air oxidation	28
4.1. Carbonaceous deposits	28
4.2. Metal leaching	28
4.3. Mitigation of catalyst deactivation	29
5. Conclusions	29
Acknowledgement	30
References	30

\* Corresponding author. Tel.: +82 42 350 3915; fax: +82 42 350 5955.

E-mail address: [skihm@kaist.ac.kr](mailto:skihm@kaist.ac.kr) (S.-K. Ihm).

## 1. Introduction

Wastewaters from industries such as pulp and paper, dyeing, chemical, petrochemical, etc. contain hazardous and refractory organic pollutants which can cause severe problems for the environment. They must be treated to satisfy the stringent water quality regulations and the demand for recycling of water in the process.

Conventional technologies including biological, thermal, and physicochemical treatments have been used to remove the aqueous pollutants. Although biological method is widely applied for the treatment of residual wastewaters, it requires a long residence time for microorganisms to degrade pollutants and is not suitable to treat the toxic contaminants due to biomass poisoning. Incineration is appropriate for the treatment of effluents having more than 100 g/L of chemical oxygen demand (COD). However, it requires an extremely high energy and presents considerable emission of other hazardous compounds such as dioxin and furan [1]. Some other techniques such as flocculation, precipitation, adsorption, air stripping, and reverse osmosis require a post-treatment to dispose of the pollutants from the newly contaminated environment [2]. The aforementioned limitations of conventional methods have encouraged the researchers to develop more efficient and environmental-friendly system for wastewater treatment.

Advanced oxidation processes (AOPs) with the capability of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds [3]. Several technologies like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals. Wet air oxidation (WAO), which was proposed and developed by Zimmermann [4], is one of the most economically and technologically viable AOPs for wastewater treatment. The application range of each AOP is different depending on the flow rate and organic content of effluent to be treated [5]. AOPs based on ozonation and wet peroxide oxidation (WPO) are preferred at low flow rates and low organic loads. Incineration is only suitable for highly concentrated wastewater at low flow rate, while biological treatments appear to be appropriate for high flow rate and low content of organic. Unlike other AOPs, WAO is proper to a high organic loading at high flow rate and can partially cover the application range of incineration and biological methods. Especially, WAO has a great potential for the treatment of effluent containing a high content of organic matter (about 10–100 g/L of COD) and/or toxic contaminants for which direct biological treatment is not feasible. By using WAO, the organic pollutants are either partially oxidized into biodegradable intermediates or mineralized to carbon dioxide, water, and innocuous end products under elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using a gaseous source of oxygen (either pure oxygen or air) as the oxidant [6]. WAO is not only eco-friendly but also economical as compared to other AOPs using harmful and expensive oxidizing agents like ozone and hydrogen peroxide.

Application of the proper catalysts for WAO process, i.e. catalytic wet air oxidation (CWAO), not only reduces the severity of reaction conditions but also more easily decomposes even refractory pollutants, thereby reducing capital and operational cost [6–18]. Though it varies with type of wastewater, the operating cost of CWAO is about half that of non-catalytic WAO due to milder operating conditions and shorter residence time [19]. Although the homogenous catalysts, e.g. dissolved copper salts, are effective, an additional separation step is required to remove or recover the metal ions from the treated effluent due to their toxicity, and accordingly increases operational costs. Thus, the development of active heterogeneous catalysts has received a great attention because a separation step is

not necessary. Various solid catalysts including noble metals, metal oxides, and mixed oxides have been widely studied for the CWAO of aqueous pollutants.

The present article reviews the recently published literature (mainly last ten years) on the heterogeneous CWAO of refractory organic pollutants including phenolics, carboxylic acids, nitrogen-containing compounds, and real wastewaters highlighting the catalytic performances and reaction conditions. Reaction mechanisms and kinetics that have been proposed for the heterogeneous CWAO of organic compounds, mainly phenol, are discussed to help the understanding of heterogeneous catalytic reaction. Finally, discussions are made on the main reason of catalyst deactivation in heterogeneous CWAO, namely carbonaceous deposits and metal leaching.

## 2. Heterogeneous catalytic wet air oxidation

Various heterogeneous catalysts including noble metals, metal oxides, and mixed oxides have been prepared and tested for the CWAO of model compounds and real wastewaters to find the new catalytic materials with high activity and stability. In this section, the studies on the heterogeneous CWAO of phenolic compounds, carboxylic acids, N-containing compounds, and real wastewaters published in the last decade are discussed, highlighting the catalytic performances and reaction conditions.

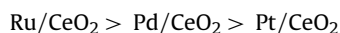
### 2.1. Catalytic wet air oxidation of phenolic compounds

Among the harmful organic compounds, phenolic substances have deserved more attention because of their toxicity and frequency of industrial wastewaters [6,20]. They give off unpleasant odor and taste even at very low concentrations [21]. Moreover, phenol is considered to be an intermediate in the oxidation pathway of higher molecular weight aromatic compounds and thus is mainly taken as a model compound for advanced wastewater treatments [22,23].

#### 2.1.1. Catalytic wet air oxidation of phenol

**2.1.1.1. Catalytic wet air oxidation of phenol over noble metal catalysts.** Noble metals such as Ru, Rh, Pd, and Pt generally show higher catalytic activity and also higher resistance to metal leaching than base metal oxide catalysts. They are usually supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and carbon materials with less than 5% of metal loading. Studies on the CWAO of phenol using noble metal catalysts are listed in Table 1.

Among the noble metals used for the CWAO of phenol, Ru is one of the most active catalysts. Pintar et al. [24] reported that the Ru/TiO<sub>2</sub> catalysts enabled complete removal of phenol and total organic carbon (TOC) without the formation of carbonaceous deposits at temperatures above 210 °C and 10 bar of oxygen partial pressure. Castillejos-Lopez et al. [25] studied the CWAO of phenol over 2 wt% Ru catalysts supported on three different supports, i.e. ZrO<sub>2</sub>, graphite, and activated carbon (AC). The use of AC as a support enhanced the phenol conversion and mineralization due to the high adsorption capacity of AC. Also, the use of RuCl<sub>3</sub> as a ruthenium precursor increased the catalytic activity and selectivity towards CO<sub>2</sub> formation, probably because the residual chlorine ions prevent the over-oxidation of ruthenium particle. Barbier et al. [26] demonstrated the activity order of CeO<sub>2</sub> supported noble metals for the CWAO of phenol as follows:



In the presence of Ru/CeO<sub>2</sub> catalyst, almost complete conversion of phenol was achieved after 3 h run under 160 °C and 20 bar of oxygen. Despite the highest initial rates of phenol conversion,

**Table 1**  
Summary of studies on CWAO of phenol over noble metal catalysts.

Catalyst	Reactor	Reaction conditions	Reference
Ru/TiO <sub>2</sub>	TBR	55–250 °C, 0–1.0 MPa of O <sub>2</sub>	[24]
Ru on ZrO <sub>2</sub> , graphite, and AC	SR	140 °C, 2.0 MPa of O <sub>2</sub>	[25]
Ru, Pd, and Pt on CeO <sub>2</sub>	SR	120–230 °C, 2.0 MPa of O <sub>2</sub>	[26]
Ru on CeO <sub>2</sub> and ZrO <sub>2</sub> -CeO <sub>2</sub>	UFBR	140 °C, 4.0 MPa of air	[27]
Ru/C and Ru-CeO <sub>2</sub> /C	SR	160 °C, 2.0 MPa of O <sub>2</sub>	[28]
Ru-CeO <sub>2</sub> on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	TBR	140 °C, 0.7 MPa of O <sub>2</sub>	[29]
Pt on graphite, TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , and AC	SR	120–170 °C, 1.7 MPa of air	[30]
Pt, Pd, and Ru on CNF	TBR	180–240 °C, 1.0 MPa of O <sub>2</sub>	[31]
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> and Pt-Ce/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	SR	155–200 °C, 5.05 MPa of air	[32]
Pt on CeO <sub>2</sub> and Ce <sub>x</sub> Zr <sub>1-x</sub> O <sub>2</sub> (x = 0.90, 0.75, and 0.50)	SR	160 °C, 2.0 MPa of O <sub>2</sub>	[33]

SR: batch or semi-batch operated stirred-tank reactors with slurry.

UFBR: continuously operated fixed-bed reactors with co-current upflow of gas and liquid phases.

TBR: continuously operated fixed-bed reactors with co-current downflow of gas and liquid phases (trickle-flow regime).

the Pd/CeO<sub>2</sub> catalyst was suddenly deactivated by coke deposition after 1 h of reaction. The Ru/CeO<sub>2</sub> catalyst was less affected by the carbonaceous deposits, and consequently showed higher phenol conversion. Wang et al. [27] reported that the introduction of ZrO<sub>2</sub> into CeO<sub>2</sub> increased the mechanical strength, specific surface area, and adsorption capacity of pelletized Ru catalysts. With the 2 wt% Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst, phenol and TOC removal stabilized approximately 100% and 96%, respectively, in a continuous packed-bubble column reactor for 100 h at 140 °C and 4 MPa of air. The addition of Ce to the Ru catalyst supported on carbon effectively enhanced the catalytic activity, and thus phenol was completely converted after 3 h reaction at 160 °C and 20 bar of O<sub>2</sub>, presumably because ceria moieties in contact with Ru particles promote the activity of Ru [28]. Massa et al. [29] investigated the effect of preparation method, i.e. impregnation, co-impregnation, co-precipitation, and surfactant, on the performance of 1% Ru–5% CeO<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the CWAO of phenol. The catalysts prepared by impregnation method were more effective and thus showed more than 90% of CO<sub>2</sub> selectivity even for low phenol conversion at 140 °C and 7 atm of O<sub>2</sub>. However, the catalysts were deactivated by the carbonaceous deposition on the active sites and the formation of boehmite phase on the support.

The CWAO of phenol with the Pt catalyst on different supports, namely graphite, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and AC was investigated by Masende et al. [30]. The graphite supported Pt catalyst was found to be most effective and stable for the CWAO of phenol. Deactivation due to over-oxidation was gradual for Pt/graphite with a metal dispersion of 5.3% as compared to Pt/TiO<sub>2</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, and Pt/AC which have much higher metal dispersion than Pt/graphite. Taboada et al. [31] reported that the Pt catalyst supported on carbon nanofiber (CNF) synthesized by catalytic chemical vapor deposition (CVD) method was very active for the CWAO of phenol but did not exhibit constant activity due to the oxidation of CNF support to CO<sub>2</sub> and unidentified organic intermediates. Kim and Ihm [32] investigated the effect of Pt precursors and Ce addition on the activity of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for the CWAO of phenol. The Pt catalysts from the anionic precursor (H<sub>2</sub>PtCl<sub>6</sub>) showed much higher activity than those from the cationic precursor (Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>) due to a better metal dispersion. Addition of Ce decreased the activity of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts from H<sub>2</sub>PtCl<sub>6</sub> due to the reduction of Pt surface area, while it improved the activity of catalysts from Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> due to the enhancement of surface reducibility by the interactions between Pt and Ce. Nouisir et al. [33] showed that the introduction of Zr into the lattice of CeO<sub>2</sub> increased significantly the mobility of oxygen atoms, especially in the presence of Pt, confirmed by oxygen storage capacity (OSC) measurements. Although the Pt catalysts on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (x = 0.90, 0.75, and 0.50) showed lower conversion of phenol and TOC than those on CeO<sub>2</sub>, the Pt/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst exhibited the highest mineralization value of 57% after 3 h reaction at 160 °C and 2 MPa of O<sub>2</sub> in a stirred batch reactor. In the case of CeO<sub>2</sub> supported cat-

alysts, the lower the surface area, the higher the mineralization values.

**2.1.1.2. Catalytic wet air oxidation of phenol over metal oxide catalysts.** Although noble metals show excellent catalytic activities as mentioned earlier, they are expensive and vulnerable to poisoning by halogen-, sulfur-, and phosphorus-containing compounds, affecting tremendously the economics of corresponding processes. Metal oxide catalysts have been widely studied as alternatives in the CWAO process even if they show rather lower activities than noble metals. Studies on the CWAO of phenol over various metal oxide catalysts are summarized in Table 2.

Among the metal oxides, Cu-based catalysts usually exhibit high activities and thus are widely used in the CWAO process. Kim and Ihm [34] studied the CWAO of phenol over transition metal (Cu, Ni, Co, Fe, and Mn) oxide catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The CuO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest catalytic activity due to its highest surface reducibility. The optimum copper loading was about 7 wt% under reaction conditions applied in their work (150 °C and 5.05 MPa of air) and the chemical states of copper in the CuO<sub>x</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were confirmed with the results of TPR, XRD, and XANES experiments as varying with copper loading: isolated Cu<sup>2+</sup> ions for 1 wt%, highly dispersed Cu<sup>2+</sup> cluster for 5 wt% and 7 wt%, and bulk CuO for 10–25 wt% [35]. Transition metal oxide catalysts on Ce<sub>0.65</sub>Zr<sub>0.35</sub>O<sub>2</sub> prepared by supercritical synthesis showed higher catalytic activities than those on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the CWAO of phenol due to the excellent redox properties of ceria-zirconia mixed oxide [36,37]. As observed in the CWAO of phenol over the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts, the CuO<sub>x</sub> catalyst was the most effective catalyst in view of catalytic activity and mineralization selectivity. It was suggested that the leached copper ions seem to contribute to the higher conversion of phenol over the CuO<sub>x</sub>/Ce<sub>0.65</sub>Zr<sub>0.35</sub>O<sub>2</sub> catalyst via homogeneous catalysis [37]. Arena et al. [38] investigated the activity and resistance to leaching of a co-precipitated CuCeO<sub>x</sub> (Cu<sub>at</sub>:Ce<sub>at</sub> = 1:9) for the CAWO of phenol, with reference to a commercial CuZnAlO<sub>x</sub> catalyst (G66A, Süd-Chemie AG). In spite of a considerably higher reducibility, the CuCeO<sub>x</sub> catalyst showed lower performance than G66A due to lower homogeneous catalytic contribution, i.e. lower concentration of leached copper ions (22 ppm) than that for G66A (66 ppm). Hocevar et al. [39] found that the activity and selectivity of the Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2- $\delta$</sub>  catalysts increased with the dispersion of copper oxide phase on cerium oxide. The catalysts prepared by sol-gel method were up to four times more active and about 25% more selective toward CO<sub>2</sub> formation than those prepared by co-precipitation.

Mesoporous silicates such as MCM-41 could be a promising catalyst support for CWAO due to their uniform pore structure and large surface area. Copper catalysts supported on mesoporous MCM-41 with surface area over 1400 m<sup>2</sup>/g were evaluated in the CWAO of phenol [40]. The results suggested that Cu/MCM-41 with

**Table 2**  
Summary of studies on CWAO of phenol over metal oxide catalysts.

Catalyst	Reactor	Reaction conditions	Reference
Cu, Ni, Co, Fe, and Mn on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	SR	150 °C, 5.05 MPa of air	[34]
1–25 wt% CuO on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	SR	150 °C, 5.05 MPa of air	[35]
Cu, Ni, Co, Fe, and Mn on Ce <sub>0.65</sub> Zr <sub>0.35</sub> O <sub>2</sub>	SR	150 °C, 5.05 MPa of air	[37]
CuCeO <sub>x</sub> (Cu <sub>at</sub> :Ce <sub>at</sub> = 1:9)	SR	150 °C, 0.7 MPa of O <sub>2</sub>	[38]
Ce <sub>1-x</sub> Cu <sub>x</sub> O <sub>2-<math>\delta</math></sub> (0.07 < x < 0.27) by co-precipitation	SR	150 °C, 0.73 MPa of O <sub>2</sub>	[39]
Ce <sub>1-x</sub> Cu <sub>x</sub> O <sub>2-<math>\delta</math></sub> (0.05 < x < 0.20) by sol-gel method			
Cu/MCM-41	SR	150 °C, 2.0 MPa of O <sub>2</sub> ; 200 °C, 3.4 MPa of O <sub>2</sub>	[40]
CeO <sub>2</sub>	SR	95–180 °C, 0.5–1.0 MPa of O <sub>2</sub>	[50]
CeO <sub>2</sub> on $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , TiO <sub>2</sub> , CeO <sub>2</sub> , and AlPO <sub>4</sub> -5	SR	140–180 °C, 1.5 MPa of O <sub>2</sub>	[51]
CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	SR	180 °C, 0.5–2.0 MPa of O <sub>2</sub>	[52]
CeO <sub>2</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub> promoted with Cu, Mn, Co, Cr, Fe, Mo, and Ni	SR	140–180 °C, 1.5 MPa of O <sub>2</sub>	[53]
MnCeO <sub>x</sub>	SR	110 °C, 0.5 MPa of O <sub>2</sub>	[54]
MnCeO <sub>x</sub> and K-promoted MnCeO <sub>x</sub>	SR	130 °C, 2.07 MPa of air	[55]
MnCeO <sub>x</sub> and K-promoted MnCeO <sub>x</sub>	SR	100 °C, 0.9 MPa of O <sub>2</sub>	[56]
MnCeO <sub>x</sub>	SR	100 °C, 0.9 MPa of O <sub>2</sub>	[57]
CeO <sub>2</sub> , TiO <sub>2</sub> , and CeO <sub>2</sub> -TiO <sub>2</sub>	SR	150 °C, 3.0 MPa of air	[59]
	UFBR	140 °C, 3.5 MPa of air	
Fe/AC	TBR	100–127 °C, 0.8 MPa of air	[60]
Fe/AC	TBR	100–114 °C, 0.8 MPa of air	[61]
Fe/AC	TBR	127 °C, 0.8 MPa of air	[62]
Fe/AC	TBR	127 °C, 0.8 MPa of air	[63]

a thin layer of copper loading should be enough to provide a high catalytic activity and a high copper loading on MCM-41 is not necessary, as it will reduce the surface area. However, a poor hydrothermal stability of mesoporous silicates is still a problem to be solved.

Ceria-based materials as a catalyst have attracted a lot of attention due to their redox and morphological properties [41–48]. Although the catalytic action in CWAO has not been totally clarified, the principal role of ceria is likely to act as a good medium for oxygen activation and transport. This characteristic is associated with the formation of oxygen defect sites and should contribute to oxygen activation by promoting production of active radicals or direct redox reaction [49]. Lin et al. [50] reported that the CeO<sub>2</sub> subjected to higher thermal impact had a less stable structure, more exchangeable structure oxygen, and more oxidizing ability. In the presence of this catalyst, phenol conversion was higher than 90% and CO<sub>2</sub> selectivity was about 80% after 4 h reaction at temperatures above 160 °C and 0.5–1.0 MPa of O<sub>2</sub>. Chen et al. [51] investigated the activities of several supported CeO<sub>2</sub> catalysts for the CWAO of phenol. The CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst had the most exchangeable structure O<sub>2</sub> and the highest H<sub>2</sub> consumption, and consequently showed the highest activity. In the presence of 20 wt% CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, approximately complete phenol conversion and 80% of COD removal were achieved after 2 h reaction under 180 °C and 1.5 MPa of oxygen. In a successive study, the optimal operating conditions for the CWAO of phenol over the CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst were estimated with respect to initial phenol concentration, oxygen partial pressure, and catalyst loading [52]. Addition of Cu to the CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst enhanced activity, and thus phenol was completely degraded for 1 h at 180 °C. In spite of the superior catalytic performance, leaching of Cu<sup>2+</sup> from the promoted catalyst caused a severe reduction in activity [53].

Introduction of transition metals into the lattice of ceria can enhance the redox property, surface area, and thermal stability mainly driven by structural modifications. Chen et al. [54] studied the CWAO of phenol over Mn-Ce-O composite catalysts with Ce/(Mn+Ce) atomic bulk ratios ranging from 0 to 1. The catalyst with Ce/(Ce+Mn) ratio of 0.4 was the most active for the removal of phenol and TOC, while pure manganese oxide was slightly active and pure cerium oxide hardly showed catalytic activity. Santiago et al. [55] investigated the effect of potassium impregnation (up to 10%) to MnO<sub>2</sub>-CeO<sub>2</sub> on catalytic performance for the CWAO of

phenol. The catalyst impregnated with 1% of K showed the highest efficiency, achieving the 90% of TOC conversion within 60 min under 130 °C and 20.4 atm. The increase in the amount of impregnated potassium adversely affected the phenol conversion due to the decrease in surface area. Arena et al. [56] reported that addition of K to the co-precipitated MnCeO<sub>x</sub> (Mn<sub>at</sub>/Ce<sub>at</sub> = 1) enhanced the catalytic activity, resulting in more than 90% of phenol and TOC conversion after 30–40 min of reaction under 100 °C and 0.9 MPa of O<sub>2</sub>. They proposed the redox-precipitation route which provided highly dispersed MnCeO<sub>x</sub> catalysts with improved physicochemical properties [56–58]. Irrespective of the Mn/Ce ratio, the redox-precipitation route ensured a large surface area, a uniform pore size distribution, and a mono-layer active phase dispersion, strongly promoting the catalytic performance for the CWAO of phenol [58]. Yang et al. [59] reported that the CeO<sub>2</sub>-TiO<sub>2</sub> mixed oxides prepared by co-precipitation method showed higher activity than pure CeO<sub>2</sub> and TiO<sub>2</sub>. The CeO<sub>2</sub>-TiO<sub>2</sub> 1/1, in which molar ratio of Ce and Ti was 1/1, exhibited the highest activity for the CWAO of phenol and resistance to the metal leaching during the 100 h of continuous reaction.

Quintanilla et al. [60,61] tested the Fe/AC catalyst for the CWAO of phenol in a down-flow fixed-bed reactor. Complete phenol conversion and 80% of TOC removal were obtained at 127 °C and 8 atm of O<sub>2</sub>. No more than 2% of initial Fe was leached out during the 9 days operation. Extended studies employing the Fe/AC catalyst pointed out significant changes in carbon during the CWAO of phenol [62,63]. After the long-term experiments, the loss of microporosity, the temporary decrease of mesoporosity, the decrease of carbon/oxygen ratio on catalyst surface, more acidic pH values, and the aggregation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystallites occurred by the formation of phenolic condensation products and the oxidation of carbon surface itself. Despite these changes in the Fe/AC catalyst, a long-term constant activity was maintained because phenol oxidation occurs mainly on the meso and macropores, and Fe acts as a promoter favoring the adsorption of oxygen.

**2.1.1.3. Catalytic wet air oxidation of phenol over carbon materials.** As previously stated, carbon materials have been widely used as a support due to their high adsorption capacity and stability in various reaction media. They also act as a catalyst for the liquid phase oxidation resulting from the catalytic properties of the surface functional groups which may be present originally or introduced by

**Table 3**  
Summary of studies on CWAO of phenol over carbon materials.

Catalyst	Reactor	Reaction conditions	Reference
AC (Sonofcarb RTA-180, Molecular Products), AC (Centaur FE80127H, Chemviron Carbon), and AC (Industrial React FE01606A, Chemviron Carbon)	UFBR	160 °C, 1.6 MPa of O <sub>2</sub>	[71]
AC (Industrial React FE01606A, Chemviron Carbon)	UFBR	160 °C, 1.6 MPa of O <sub>2</sub>	[72]
MWCNT	SR	160 °C, 2.0 MPa of O <sub>2</sub>	[73]

specific chemical modifications [64–66]. Studies on the CWAO of phenol over carbon materials are listed in Table 3.

AC without metal impregnation seems to be a promising catalyst for the CWAO of organic pollutants. It is relatively cheap and avoids the leaching problem due to its high stability in both acidic and alkaline environments [67–70]. Santos et al. [71] suggested that the main advantages of AC as a catalyst for CWAO are the poor selectivity in oxidation yielding higher mineralization of pollutants, and no leaching of active phase because the metal impregnation is not required. Cordero et al. [72] reported that a commercial AC (Industrial React FE01606A, Chemviron Carbon) showed an initial loss of activity with time on stream reaching a steady state (70% of phenol and 40% of TOC conversion) at about 50 h reaction due to the decrease in surface area of micropore, while the external surface area and the total amount of oxygen surface group increased as reaction proceeded. The total micropore volume and internal surface area of catalyst were not recovered by regeneration, probably due to the blockage of narrow micropores by pyrolytic carbon formed from the first step of CWAO.

Multi-walled carbon nanotubes (MWCNT) chemically modified using HCl or HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> exhibited a high activity and a good stability for the CWAO of phenol [73]. Complete phenol conversion and 76% of TOC removal were achieved after 120 min reaction at 160 °C and 2 MPa of O<sub>2</sub>. Increasing the reflux time for MWCNT could lead to produce the higher concentration of surface functional groups (-COOH) which should play a key role in the high activity of functionalized MWCNT.

### 2.1.2. Catalytic wet air oxidation of substituted phenol

Some of studies on the CWAO of substituted phenol are summarized in Table 4. Supported noble metals have been tested for the CWAO of phenol substituted with chlorine. Qin et al. [74] compared the activity of noble metals (Pd, Pt, and Ru) supported on AC,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> for the CWAO of *p*-chlorophenol. They reported the Pt as the most active metal and AC as the most active support for *p*-chlorophenol oxidation. The activities of noble metal catalysts were found to correlate with the heat of formation of metal oxides. Li et al. [75,76] studied the CWAO of *o*-chlorophenol over Ru/ZrO<sub>2</sub> and Ru/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts. The results demonstrated that the conversion of *o*-chlorophenol increased with the initial pH value due to the acceleration of dechlorination, while too high pH value

limited the total mineralization of *o*-chlorophenol by preventing the adsorption of reaction intermediates. It was also confirmed that Ru(NO)(NO<sub>3</sub>)<sub>3</sub> was better than RuCl<sub>3</sub> to act as a ruthenium precursor [75]. The Ru catalysts on Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> exhibited higher performances than those on CeO<sub>2</sub> and ZrO<sub>2</sub>. Furthermore, the introduction of small amount of Pr or Nd into the Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> lattice improved the activity of Ru/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts where Pr showed a greater effect than Nd [76]. Yamada et al. [77] found that the alkaline reagent (NaOH) played an important role in dechlorination of *o*-chlorophenol. The decomposition of *o*-chlorophenol over the Ru/TiO<sub>2</sub> catalyst occurred most effectively at the initial pH of 9.8 under 140 °C and 0.1 MPa of O<sub>2</sub>, and thus almost complete conversion and dechlorination of *o*-chlorophenol were obtained within 1 h. A higher pH value of 11.8, on the other hand, was not effective in the removal of TOC due to a low pK<sub>a</sub> of carboxylic acids formed during the CWAO of *o*-chlorophenol [78].

The performance of 4 wt% Cu/CeO<sub>2</sub> catalyst for the CWAO of phenol, *o*-chlorophenol, and *p*-nitrophenol was investigated by Posada et al. [79]. Under 160 °C and 1 MPa, complete conversion of phenol and *o*-chlorophenol were achieved after 100 min and 130 min, respectively, but only about 60% of *p*-nitrophenol was degraded after 200 min. The Cu catalyst on CeO<sub>2</sub> showed much higher activity than that on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> presumably due to the synergistic effect of copper oxide and the surface oxygen vacancies of ceria by means of the formation of interfacial active centers. The 54.5 mg/L of Cu<sup>2+</sup> ions was detected in the treated solution and should be partially responsible of high conversion over the Cu/CeO<sub>2</sub> catalyst through homogeneous contribution. The CWAO treatment improved the biodegradability of three phenolic compounds, confirmed with the increase of the BOD<sub>5</sub>/COD ratio.

Commercial ACs have been used as a catalyst for the CWAO of various phenolic compounds. Suarez-Ojeda et al. [80] performed the CWAO of *o*-chlorophenol, phenol, sodium dodecylbenzene sulfonate (DBS), *o*-cresol, aniline, sulfolane, *p*-nitrophenol, and nitrobenzene using a commercial AC supplied by Merck at 140 °C and 13.1 bar of air in a trickle-bed reactor. They suggested that the reactivity order, *o*-chlorophenol > phenol > DBS > *o*-cresol > aniline, sulfolane, seems to correspond to a nucleophilic aromatic substitution mechanism. In their consecutive study, the results showed that the pollutant conversion, distribution of partial oxidation products, and biodegradability were very sensitive to tempera-

**Table 4**  
Summary of studies on CWAO of substituted phenol.

Catalyst	Substituted phenol	Reactor	Reaction conditions	Reference
Pd, Pt, and Ru on AC, $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , and CeO <sub>2</sub>	<i>p</i> -chlorophenol	SR	180 °C, 2.6 MPa of air	[74]
Ru/ZrO <sub>2</sub>	<i>o</i> -chlorophenol	SR	130–160 °C, 2.0–6.0 MPa of air	[75]
Ru on Ce <sub>x</sub> Zr <sub>1-x</sub> O <sub>2</sub> , Ce-Zr-PrO <sub>x</sub> , and Ce-Zr-NdO <sub>x</sub>	<i>o</i> -chlorophenol	SR	120–140 °C, 3.0–5.0 MPa of air	[76]
Ru/TiO <sub>2</sub>	<i>o</i> -chlorophenol	SR	100–160 °C, 0.1 MPa of O <sub>2</sub>	[77]
Ru/TiO <sub>2</sub>	<i>o</i> -chlorophenol	SR	100–140 °C, 0.1 MPa of O <sub>2</sub>	[78]
Cu/CeO <sub>2</sub>	<i>o</i> -chlorophenol and <i>p</i> -nitrophenol	SR	160 °C, 1.0 MPa of air	[79]
AC (#102518, Merck)	<i>o</i> -cresol, <i>o</i> -chlorophenol, and <i>p</i> -nitrophenol	TBR	140 °C, 1.31 MPa of air	[80]
AC (#102518, Merck)	<i>o</i> -cresol and <i>o</i> -chlorophenol	TBR	140–160 °C, 0.2–0.9 MPa of O <sub>2</sub>	[81]
AC (Industrial React FE01606A, Chemviron Carbon)	<i>o</i> -cresol, <i>p</i> -cresol, <i>o</i> -nitrophenol, and <i>p</i> -nitrophenol	UFBR	160 °C, 1.6 MPa of O <sub>2</sub>	[82]
Pt and Ru on TiO <sub>2</sub> and ZrO <sub>2</sub>	<i>p</i> -hydroxybenzoic acid	SR	140 °C, 5.0 MPa of air	[87]
Ru on TiO <sub>2</sub> and ZrO <sub>2</sub>	<i>p</i> -hydroxybenzoic acid	SR, TBR	140 °C, 5.0 MPa of air	[88]
Ru/TiO <sub>2</sub>	<i>p</i> -hydroxybenzoic acid	SR	140 °C, 5.0 MPa of air	[89]
Ru on CeO <sub>2</sub> , TiO <sub>2</sub> , and CeO <sub>2</sub> -TiO <sub>2</sub>	<i>p</i> -hydroxybenzoic acid	SR	140 °C, 5.0 MPa of air	[90]
LaFeO <sub>3</sub>	salicylic acid	SR	100–180 °C, 0.5 MPa of O <sub>2</sub>	[91]

**Table 5**  
Summary of studies on CWAO of carboxylic acids.

Catalyst	Carboxylic acid	Reactor	Reaction conditions	Reference
Ru/TiO <sub>2</sub>	Acetic acid	TBR	55–250 °C, 0–1.0 MPa of O <sub>2</sub>	[24]
RuO <sub>2</sub> on ZrO <sub>2</sub> , CeO <sub>2</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub> –CeO <sub>2</sub> , and TiO <sub>2</sub> –CeO <sub>2</sub>	Acetic acid	SR	200 °C, 4.0 MPa of air	[92]
CeO <sub>2</sub> –TiO <sub>2</sub>	Acetic acid	SR	230 °C, 5.0 MPa of air	[95]
Ru on CeO <sub>2</sub> and Zr <sub>0.1</sub> (Ce <sub>0.75</sub> Pr <sub>0.25</sub> ) <sub>0.9</sub> O <sub>2</sub>	Acetic acid	SR	200 °C, 2.0 MPa of O <sub>2</sub>	[96]
Pt and Ru on CeO <sub>2</sub> , Zr <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>2</sub> , and Zr <sub>0.1</sub> (Ce <sub>0.75</sub> Pr <sub>0.25</sub> ) <sub>0.9</sub> O <sub>2</sub>	Acetic acid	SR	200 °C, 2.0 MPa of O <sub>2</sub>	[97]
Pt on CeO <sub>2</sub> , ZrO <sub>2</sub> , Zr <sub>0.1</sub> Ce <sub>0.9</sub> O <sub>2</sub> , and Zr <sub>0.1</sub> (Ce <sub>0.75</sub> Pr <sub>0.25</sub> ) <sub>0.9</sub> O <sub>2</sub>	Acetic acid	SR	200 °C, 2.0 MPa of O <sub>2</sub>	[98]
Pt on CeO <sub>2</sub> and Zr <sub>0.1</sub> (Ce <sub>0.75</sub> Pr <sub>0.25</sub> ) <sub>0.9</sub> O <sub>2</sub>	Acetic acid	SR	200 °C, 2.0 MPa of O <sub>2</sub>	[99]
Pt/C	Acetic acid, propionic acid, and butyric acid	SR	200 °C, 0.69 MPa of O <sub>2</sub>	[100]
Pt/γ-Al <sub>2</sub> O <sub>3</sub>	Maleic acid, oxalic acid, and formic acid	SR	80–180 °C, atmospheric pressure–1.1 MPa of air	[101]
Ru, Pd, Pt, and Ir on CeO <sub>2</sub>	Stearic acid	SR	160–230 °C, 0.1–2.0 MPa of O <sub>2</sub>	[103]
La <sub>1-x</sub> A <sub>x</sub> BO <sub>3</sub> (A' = Sr, Ce; B = Co, Mn)	Stearic acid	SR	200 °C, 2.0 MPa of O <sub>2</sub>	[104]

ture but almost independent of the oxygen partial pressure, while AC preservation was strongly influenced by both of them [81]. Santos et al. [82] studied the CWAO of phenol, *o*-cresol, *p*-cresol, *o*-nitrophenol, and *p*-nitrophenol with a commercial AC (Industrial React FE01606A, Chemviron Carbon) in both acid and basic conditions. While hydroxybenzoic acids, dihydroxyl benzenes, and quinones were detected as primary products in acidic conditions, these last two compounds which are more toxic than original compound were not observed in basic conditions. During the reaction, the AC showed changes in its initial texture due to the oxidation of external surface and its original physicochemical properties, namely a remarkable reduction of BET surface area.

*p*-Hydroxybenzoic acid has attracted a special interest because it is typically found in the effluent from olive oil industry [83] and is also observed as an unexpected intermediate of phenol oxidation over AC [84,85]. *p*-Hydroxybenzoic acid is especially toxic and refractory to biological treatment [86]. Minh et al. [87] carried out the CWAO of *p*-hydroxybenzoic acid using the noble metals (Ru and Pt) supported on ZrO<sub>2</sub> and TiO<sub>2</sub>. They found that *p*-hydroxybenzoic acid was oxidized through hydroxylation and decarboxylation to produce phenol and hydroquinone which were further mineralized via maleic acid. For the supported Ru catalysts, the use of a non-chlorine ruthenium precursor, i.e. Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, provided a significant metal dispersion and an efficient surface accessibility. A little deactivation was observed during the first recycling of Ru catalyst in a batch reactor, which was totally reversible after catalyst reduction. Moderate deactivation was also observed at the start of continuous runs due to the over-oxidation of surface or sub-surface of Ru particles. During the fifty days long-term runs in a trickle-bed reactor, the Ru catalysts maintained their activity without metal leaching [88]. Triki et al. [89] suggested the Ru supported on TiO<sub>2</sub> aerogels as an effective catalyst for the CWAO of *p*-hydroxybenzoic acid and investigated the some preparation parameters to optimize the catalytic performance. The results showed that the use of incipient wetness impregnation method, nitric acid as a hydrolysis agent, and Ru(NO)(NO<sub>3</sub>)<sub>3</sub> as a metal precursor led to the optimal catalyst with a significant metal dispersion and the highest TOC abatement, while the calcination of catalyst precursor before reduction adversely affected the catalytic performance. Triki et al. [90] also applied the CeO<sub>2</sub>–TiO<sub>2</sub> as a support of Ru catalysts for the CWAO of *p*-hydroxybenzoic acid. It was found that the decrease in the molar ratio of Ce/Ti from 3 to 1/3 improved the activity of Ru catalysts. The Ru/CeO<sub>2</sub>–TiO<sub>2</sub> catalyst exhibited higher activity than Ru/CeO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts due to the synergy effect between ceria and titania, affecting the surface structural properties of CeO<sub>2</sub>–TiO<sub>2</sub> support.

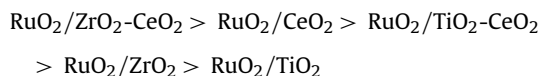
A perovskite-type LaFeO<sub>3</sub> catalyst prepared by sol–gel method was applied to the CWAO of salicylic acid (2-hydroxybenzoic acid) which is an important raw material for various organic compounds, dyes, pharmaceuticals, plasticizers, antioxidants, etc. [91]. It was

discovered that the acid strength of model compound may play a key role in its degradation. With the role of hard acidity of intramolecular hydrogen bonding between carboxyl group and hydroxyl group, salicylic acid can be adsorbed effectively on the basic center of the LaFeO<sub>3</sub> catalyst and thus are easy to take place the total oxidation.

## 2.2. Catalytic wet air oxidation of carboxylic acids

Carboxylic acids are valuable commercial products and are widely used in various synthetic organic products. Short-chain carboxylic acids, mainly acetic acid, are detected as intermediates in the CWAO of aromatic compounds and are usually refractory to further oxidation. Noble metal catalysts have been typically applied to the CWAO of carboxylic acids due to their higher activity. Table 5 summarizes the studies on the CWAO of carboxylic acids.

Among the carboxylic acids, acetic acid is usually employed as a model compound because it is most refractory to mineralization. Pintar et al. [24] carried out the CWAO of acetic acid using various Ru/TiO<sub>2</sub> catalysts and found that the liquid-phase oxidation of acetic acid was structure sensitive. The Ru catalyst with a high ratio of zero-valent state showed the highest activity for the CWAO of acetic acid, and thus more than 95% of TOC removal was attained at 230 °C and 10 bar of oxygen. Wang et al. [92] reported the activity order of Ru catalysts on different supports for the CWAO of acetic acid at 200 °C and 4 MPa as follows:



which corresponded to the surface concentration of non-lattice oxygen (defect-oxide or hydroxyl-like group) of the catalysts confirmed with the XPS O1s spectra. Non-lattice oxygen on the catalyst surface has a higher mobility than lattice oxygen, and accordingly can take an active part in oxidation process [54]. It is considered to react with organic substance directly [93,94] or facilitate electron transfer to produce radicals and promote the oxidation process [43,93]. Yang et al. [95] reported that the activity of CeO<sub>2</sub>–TiO<sub>2</sub> catalysts for the CWAO of acetic acid was much higher than that of TiO<sub>2</sub> and CeO<sub>2</sub> because the addition of Ti to CeO<sub>2</sub> led to the higher content of chemisorbed oxygen and the low valence of Ce<sup>3+</sup> on the surface. Gašlová et al. [96] demonstrated that the oxygen transfer from gas phase to active site was strongly improved by doping of ceria support by other cations. Mikulová et al. [97–99] reported that the performance of Pt catalysts on ceria-based materials for the CWAO of acetic acid was dependent on the resistance of support to the formation of carbonates (Ce(CO<sub>3</sub>)OH) which substantially reduced catalytic activity, and a moderate OSC was required to maintain a good catalytic performance.

**Table 6**  
Summary of studies on CWAO of aniline.

Catalyst	Reactor	Reaction conditions	Reference
Ru/CeO <sub>2</sub>	SR	120–230 °C, 2.0 MPa of O <sub>2</sub>	[111]
Ru, Pd, and Pt on CeO <sub>2</sub>	SR	120–230 °C, 2.0 MPa of O <sub>2</sub>	[26]
Ru/SiO <sub>2</sub>	SR	175–220 °C, 0.34–1.38 MPa of O <sub>2</sub>	[112]
Ru/MWCNT	SR	200 °C, 5.0 MPa of air	[113]
Pt/MWCNT	SR	200 °C, 0.69 MPa of O <sub>2</sub>	[114]
Mesoporous carbon xerogel	SR	200 °C, 0.69 MPa of O <sub>2</sub>	[115]
Cu, Cr, and V modified MCM-41	SR	200 °C, 0.69 MPa of O <sub>2</sub>	[116]
Nanocasted Mn-Ce-oxide	TBR	110–140 °C, 1.0 MPa of O <sub>2</sub>	[117]

The CWAO of low molecular weight carboxylic acids, namely acetic acid, propionic acid, and butyric acid, using 1 wt% Pt/C catalysts was investigated by Gomes et al. [100]. The catalyst prepared by incipient wetness impregnation method showed higher activity than that by CVD due to higher metal dispersion. Using this catalyst, the conversion of butyric, propionic, and acetic acids were about 75%, 96%, and 93%, respectively, after 8 h of run at 200 °C and 6.9 bar of O<sub>2</sub>. Lee and Kim [101] carried out the CWAO of three carboxylic acids, i.e. maleic acid, oxalic acid, and formic acid, in a batch reactor. With the Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, oxalic acid and formic acid were readily oxidized into CO<sub>2</sub> and H<sub>2</sub>O at 80 °C and atmospheric pressure, while maleic acid was hardly oxidized. The presence of sulfonated poly(styrene-co-divinylbenzene) resin catalyst together with the Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalyst enhanced the degradation of maleic acid by hydrolyzing maleic acid into more readily oxidizable compounds.

Fatty acids such as stearic acid generally make the refractory products for the biological treatment of food industry effluents due to their low solubility. Saturated fatty acids are more refractory than unsaturated ones, and consequently a high temperature of 240 °C is usually necessary to significantly remove them without catalyst [102]. Renard et al. [103] carried out the CWAO of stearic acid over the noble metals (Ru, Pd, Pt, and Ir) supported on CeO<sub>2</sub> in a batch reactor. They reported that stearic acid can be oxidized by successive decarboxylation ( $R_n\text{-COOH} + \text{O}_2 \rightarrow R_{n-1}\text{-COOH} + \text{CO}_2$ ) and also be oxidized after the C–C bond cleavage within alkyl chain, which gives rise to significant amounts of acetic acid besides carbon dioxide. The Pt/CeO<sub>2</sub> catalyst was a very effective catalyst in the destruction of stearic acid and extremely selective to CO<sub>2</sub> (more than 95% of mineralization after 3 h oxidation at 200 °C and 2 MPa), while the C–C bond splitting was much more noticeable on the Ru/CeO<sub>2</sub> catalyst. Royer et al. [104] studied the CWAO of stearic acid over the transition metal-based perovskite catalysts synthesized by reactive grinding in which perovskite crystallization occurred near ambient temperature by mechanical grinding energy. LaCoO<sub>3</sub> exhibited much higher activity than Mn-based perovskites and LaCoO<sub>3</sub> with the highest OSC value showed the highest initial activity. A direct relationship between the reducibility at low temperature (OSC value) and the initial catalytic activity clearly showed that the reactivity of redox couple (either Co<sup>3+</sup>/Co<sup>2+</sup> or Mn<sup>4+</sup>/Mn<sup>3+</sup>) determined the initial catalytic activity. The formation of stable carbonate with lanthanum destroyed the perovskite structure, resulting in a decrease in reaction sites, and consequently in catalytic activity.

### 2.3. Catalytic wet air oxidation of N-containing compounds

Nitrogen-containing compounds present a very high toxicity and cause the acidification and eutrophication of ecosystems [105,106]. The oxidation of N-containing organic compounds like aniline generates phenol as a key component and acetic acid as the most refractory intermediate [14,26,107–109]. Ammonia generated from the oxidation of nitrogenous compounds is pointed out as another refractory by-product to further oxidation [14,107].

#### 2.3.1. Catalytic wet air oxidation of aniline

Aniline is a representative compound of N-containing aromatic compounds and is mainly used as a chemical intermediate in the production of polymers, pesticides, pharmaceuticals, and dyes [110]. Aniline is found to be more resistant to biodegradation than phenol. Heterogeneous CWAO is one of the most attractive technologies for the treatment of aniline. Summary of studies on the CWAO of aniline are listed in Table 6.

Barbier et al. [111] reported that at higher temperature than 150 °C, the N–C bond cleavage led to large amounts of ammonium ions during the CWAO of aniline over the Ru/CeO<sub>2</sub> catalyst. Ammonium ions were oxidized quite selectively into molecular nitrogen in the temperature range from 180 to 200 °C, while the reaction pathway was significantly oriented towards the formation of undesirable nitrite and nitrate ions above 200 °C. Barbier et al. [26] also investigated the CWAO of aniline with noble metals (Ru, Pd, and Pt) supported on CeO<sub>2</sub>. The order of activity for aniline oxidation was Ru > Pd > Pt at 160 °C and Ru > Pt > Pd at 200 °C. Despite an excellent activity, the Ru/CeO<sub>2</sub> catalyst showed the highest rate of coke deposition. At 160 °C, the Ru/CeO<sub>2</sub> catalyst showed the highest selectivity to ammonia and the Pd/CeO<sub>2</sub> catalyst exhibited the highest selectivity to molecular nitrogen. At 200 °C, the Pd/CeO<sub>2</sub> catalyst remained the most selective catalyst to molecular nitrogen, while the Ru and Pt catalysts produced significant amounts of nitrite and nitrate ions. Reddy and Mahajani [112] reported that the optimum temperature for the formation of molecular nitrogen was between 200 and 210 °C in the CWAO of aniline over the 5% Ru/SiO<sub>2</sub> catalyst. While more ammonium ions were formed below 200 °C, more nitrate ions were generated above 210 °C due to the harsh oxidizing conditions. The conversion of –NH<sub>2</sub> to molecular nitrogen increased by the addition of free radical initiator (hydroquinone), while that decreased by adding the free radical scavenger (gallic acid).

Garcia et al. [113] investigated the effect of ruthenium precursor, impregnation method, and surface chemistry of MWCNT on the performance of Ru/MWCNT for the CWAO of aniline. The experimental results demonstrated that the best compromise was the Ru catalyst supported on the Na<sub>2</sub>CO<sub>3</sub> ion exchanged MWCNT-COONa prepared from ruthenium trichloride precursor by excess solution impregnation, showing the highest dispersion, good activity, and best stability. Garcia et al. [114] also found that the Pt/MWCNT catalyst prepared from H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O showed the highest selectivity to non-organic compounds for the CWAO of aniline.

Mesoporous carbon xerogels were suggested as a promising catalyst for the CWAO of aniline by Gomes et al. [115]. Mesoporous carbon xerogel with a significant amount of oxygen functional groups showed higher catalytic activity than a commercial AC (ROX 0.8, Norit) due to its high mesoporosity favoring the adsorption and degradation of large molecules. Aniline was completely removed with the high selectivity to non-organic compounds after 1 h oxidation at 200 °C and 6.9 bar of O<sub>2</sub>. Gomes et al. [116] also reported that the Cu-anchored MCM-41 showed a significant catalytic activity with the aniline conversion of 96% and the TOC reduction of 72.9% after 2 h of reaction at 200 °C and 6.9 bar of oxygen. This catalyst exhibited a good activity and stability in three consecu-

**Table 7**  
Summary of studies on CWAO of dyes.

Catalyst	Dye	Reactor	Reaction conditions	Reference
Cu/CNF	Acid Orange 7, Acid Orange 74, Direct Blue 71, Reactive Black 5, and Eriochrome Blue Black B	SR	140 °C, 0.87 MPa of O <sub>2</sub>	[120]
AC (Industrial React FE01606A, Chemviron Carbon)	Orange G, Methylene Blue, and Brilliant Green	UFBR	160 °C, 0.16 MPa of air	[121]
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> and Na <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	Acid Orange 7	SR	160–290 °C, 0.6–3.0 MPa of air	[124]
Zn <sub>1.5</sub> PMo <sub>12</sub> O <sub>40</sub>	Safranin-T	Glass reactor	room temperature, atmospheric pressure	[125]
ZnO/MoO <sub>3</sub>	Safranin-T	Glass reactor	room temperature, atmospheric pressure	[126]
Fe <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> -TiO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Methyl Orange	Glass reactor	room temperature, atmospheric pressure	[127]
CuO-MoO <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	Methylene Blue	Glass reactor	35 °C, atmospheric pressure	[128]

tive cycles, although small amount of leached copper ions were detected.

Levi et al. [117] studied the CWAO of aniline using the nanocasted Mn-Ce-oxide catalyst ( $S_{\text{BET}} = 300 \text{ m}^2/\text{g}$ ) prepared by using SBA-15 as a hard template. With this catalyst, complete aniline conversion, a 90% of TOC conversion, and a 80% of nitrogen mineralization were achieved at 140 °C and 10 bar of oxygen in a trickle-bed reactor with liquid hourly space velocity (LHSV) of  $5 \text{ h}^{-1}$ . However, the catalyst was rapidly deactivated due to the metal leaching caused by complexation with aniline. Acidification of solution with HCl was necessary to avoid the colloidization and the leaching of nanoparticulate catalyst components.

### 2.3.2. Catalytic wet air oxidation of dyes

Removal of dyes in textile wastewater has attracted a lot of interest because of the growing concern about residual color which is closely associated with toxicity and aesthetics of the discharged effluent. Dyes exhibit a high resistance to microbial degradation because they retain color and structural integrity under exposure to sunlight, soil, and bacteria. In particular, azo dyes are readily converted to hazardous aromatic amines under anoxic conditions [118,119]. Some studies on the CWAO of dyes are summarized in Table 7.

Rodríguez et al. [120] studied the CWAO of several azo dyes (Acid Orange 7 (AO7), Acid Orange 74 (AO74), Direct Blue 71 (DB71), Reactive Black 5 (RB5), and Eriochrome Blue Black B (EBBB)) over the Cu/CNF catalyst. They reported that the treatment of CNF with acid oxidant such as HNO<sub>3</sub> introduced oxygen surface complexes to act as anchoring centers, changing the surface chemistry. At 140 °C and 8.7 bar of O<sub>2</sub>, all of azo dyes were completely degraded after 3 h reaction. Mono-azo dyes were more easily decomposed than di-azo and tri-azo dyes. The order of color removal for mono-azo dyes was EBBB > AO7 > AO74.

Santos et al. [121] studied the CWAO of three dyes commonly found in textile wastewaters, Orange G (OG), Methylene Blue (MB), and Brilliant Green (BG), with a commercial AC (Industrial React FE01606A, Chemviron Carbon). Although complete dye removal and colorless effluents were obtained at 160 °C and 16 bar of O<sub>2</sub> in a fixed-bed reactor, complete mineralization was not achieved due to the formation of intermediates. While non-toxic effluent was obtained in the CWAO of OG, the CWAO of BG exhibited the highest toxicity due to the formation of nitrogen-containing aromatic intermediates.

Heteropolyacids (HPAs) also named polyoxometalates (POMs) are oxo-clusters of early transition metals in the highest oxidation state, namely Mo (VI), W (VI), V (V), etc., which represent an important class of eco-friendly catalysts. POMs catalyze the oxidation of organic compounds under mild conditions due to their formidable structural diversity and specific properties including nano-sized dimension, shape, density, and surface reactivity [122,123]. Keggin-type polyoxotunstates (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and Na<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>) decreased significantly the activation energy for the CWAO of Acid Orange 7

and shifted the oxidation mechanism from a free radical chain reaction to an electron transfer [124]. Zhang et al. [125] reported the excellent catalytic activity of polyoxomolybdate (Zn<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub>) with nanotube structure for the CWAO of Safranin-T, in which a 98% of color and a 95% of COD were removed within 40 min under room temperature and atmospheric pressure. Safranin-T was totally mineralized to simple inorganic species such as HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. The Zn<sub>1.5</sub>PMo<sub>12</sub>O<sub>40</sub> catalyst kept stable under different cycling runs and leaching effect was negligible. The CWAO of Safranin-T under room conditions was also studied by Huang et al. [126]. With the ZnO/MoO<sub>3</sub> nanotube catalyst, the color and COD of Safranin-T were almost completely removed after 18 min and total mineralization was obtained simultaneously.

There are some works on the CWAO of azo dyes under room conditions. Liu and Sun [127] reported that the Fe<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst prepared by consecutive impregnation exhibited a high catalytic activity without metal leaching for the CWAO of Methyl Orange. Within 2.5 h, a 98.09% of color and a 96.08% of TOC were removed under room temperature and atmospheric pressure. Ma et al. [128] reported that the color removal of Methylene Blue was attained to 99.26% within 10 min under 35 °C and atmospheric pressure in the presence of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> catalyst synthesized by a solid-state reaction method. Catalyst activity almost kept constant in three consecutive runs.

### 2.3.3. Catalytic wet air oxidation of ammonia

Ammonia is widely used as a chemical in the manufacture of ammonium nitrate, metallurgy, petroleum refineries, etc. It is known as a key intermediate in the oxidation of N-containing compounds and is not amenable to direct biological treatment due to its toxicity. CWAO is very effective for the removal of ammonia, in which ammonia is mainly converted to molecular nitrogen [111,129–134]. Studies on the CWAO of ammonia are summarized in Table 8.

Lee et al. [135] elucidated the role of catalyst and the reason for the preferential formation of molecular nitrogen (N<sub>2</sub>) in the CWAO of ammonia over the Ru/TiO<sub>2</sub> catalyst. It was verified that the catalyst had no direct relevance to the selective formation of N<sub>2</sub> but was responsible only for the oxidation of ammonia, finally giving a nitrous acid (HNO<sub>2</sub>). The preferential production of N<sub>2</sub> was due to the homogeneous reaction of nitrous acid-dissociated NO<sub>2</sub><sup>-</sup> with ammonium ions (NH<sub>4</sub><sup>+</sup>). Even under the highly oxidizing condition, NO<sub>2</sub><sup>-</sup> was much more likely to react with NH<sub>4</sub><sup>+</sup> to form N<sub>2</sub> than being oxidized over catalyst to NO<sub>3</sub><sup>-</sup> as long as NH<sub>4</sub><sup>+</sup> was available in solution. To maximize the formation of N<sub>2</sub> instead of hazardous NO<sub>3</sub><sup>-</sup> in the CWAO of ammonia, it was important to adjust the solution pH at the end of the reaction to be around the neutral.

The CWAO of ammonia over the mono- and bi-metallic noble metal catalysts (Pt, Ru, and Pd) supported on cerium oxides was carried out by Barbier et al. [111]. The Pt catalyst showed higher activity than Pd and Ru. Although the Pd catalyst showed lower initial rate than the Pt catalyst, the Pd catalyst exhibited the highest



**Table 8**  
Summary of studies on CWAO of ammonia.

Catalyst	Reactor	Reaction conditions	Reference
Ru/TiO <sub>2</sub>	SR	200 °C, 0.5 MPa of O <sub>2</sub>	[135]
Pt, Ru, Pd, and Ru-Pd on CeO <sub>2</sub>	SR	120–230 °C, 2.0 MPa of O <sub>2</sub>	[111]
Pt-Pd-Rh composite washcoated on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	TBR	150–230 °C, 2.0 MPa of O <sub>2</sub>	[136]
Cu-La-Ce composite	SR	230 °C, 4.0 MPa of O <sub>2</sub>	[137]
	TBR	150–230 °C, 2.0 MPa of O <sub>2</sub>	
Cu-La-Ce composite coated on cordierite	TBR	150–200 °C, 3.0 MPa of O <sub>2</sub>	[139]
Cu/ACF	TBR	150–190 °C, 3.0 MPa of O <sub>2</sub>	[141]
Cu/ACF	TBR	150–190 °C, 2.0–5.0 MPa of O <sub>2</sub>	[142]
Co-precipitated transition metal-aluminium catalyst (transition metal: Cu, Ni, Co, Fe, and Mn)	SR	230 °C, 2.0 MPa of air	[147]
Ni/Al <sub>2</sub> O <sub>3</sub>	SR	230 °C, 2.0 MPa of air	[148]

selectivity of more than 90% towards molecular nitrogen. Co-impregnation of Ru and Pd significantly enhanced the selectivity to molecular nitrogen, while no synergy effect on ammonia conversion was observed. Although the operation at high pressures increased the solubility of oxygen and provided a strong driving force for oxidation, the formation of nitrite and nitrate ions increased with pressure, resulting in slowly deactivating the catalyst. Hung [136] applied the nanoscale Pt-Pd-Rd (weight ratio of 4:3:1) composite oxide catalyst washcoated on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the CWAO of ammonia. At 230 °C and 2 MPa of oxygen, ammonia was almost completely removed and molecular nitrogen was the main product. The results also showed that ammonia conversion at basic condition (pH 12) was much higher than that at acidic condition (pH 2). At higher solution pH, molecular ammonia favors a higher NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> ratio in the aqueous solution, and accordingly the heterogeneously catalyzed reaction on catalyst surface should be significantly occurred because NH<sub>3</sub> is more reactive than NH<sub>4</sub><sup>+</sup> [130].

Hung and co-workers [137–139] studied the CWAO of ammonia over the Cu-La-Ce composite metal catalysts. The catalyst with a Cu-La-Ce molar ratio of 7:2:1 was found to be optimal in terms of ammonia conversion [137]. It was suggested that copper (II) oxide plays an important role in the CWAO of ammonia, while lanthanum (III) and cerium (IV) oxide may serve only to provide active sites [138]. Kundakovic and Flytzani-Stephanopoulos [140] demonstrated that copper is more stable when dispersed in the Ce(La)O<sub>2</sub> matrix, and copper clusters formed on a support appear to be the most active component. With the Cu-La-Ce composite coated on cordierite, around 91% of ammonia was removed at 473 K and 3 MPa of O<sub>2</sub> in a continuous trickle-bed reactor (LHSV = 5.4 h<sup>-1</sup>) [139]. Hung [141,142] also studied the CWAO of ammonia using the Cu catalyst on activated carbon fiber (ACF) which has attracted great attention due to small fiber diameters, a large contact surface

**Table 9**  
Summary of studies on CWAO of industrial wastewaters.

Catalyst	Industrial wastewater	Reactor	Reaction conditions	Reference
TiO <sub>2</sub> , ZrO <sub>2</sub> , Ru/TiO <sub>2</sub> , and Ru/ZrO <sub>2</sub>	Kraft bleaching plant effluents	SR	190 °C, 5.5 MPa of air	[149]
TiO <sub>2</sub> and Ru/TiO <sub>2</sub>	Kraft bleaching plant effluents	TBR	190 °C, 5.5 MPa of air	[150]
TiO <sub>2</sub> and Ru/TiO <sub>2</sub>	Kraft bleaching plant effluents	SR	190 °C, 5.5 MPa of air	[151]
Pt and Ru on TiO <sub>2</sub> and ZrO <sub>2</sub>	Olive oil mill wastewater	SR and TBR	140–190 °C, 5.0–7.0 MPa of air	[152]
Pt and Ir on C	Olive oil mill wastewater	SR	100–200 °C, 0.69 MPa of O <sub>2</sub>	[153]
Ru/TiO <sub>2</sub>	Coke plant wastewater	UFBR	250 °C, 4.8 MPa of air	[154]
Ce-Cu and Ce-Mn on TiO <sub>2</sub> , $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , and $\gamma$ -Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	Coke plant wastewater	SR	140–220 °C, 1.2 MPa of O <sub>2</sub>	[155]
Cu/CNF	Textile wastewater	SR	120–160 °C, 0.63–0.87 MPa of O <sub>2</sub>	[156]
Pt/Al <sub>2</sub> O <sub>3</sub> , Mn/Ce oxides, and Cu(II)-exchanged NaY zeolite	Alcohol-distillery wastewater	SR	180–250 °C, 0.5–2.5 MPa of O <sub>2</sub>	[157]
CeO <sub>2</sub> and SiO <sub>2</sub> -doped CeO <sub>2</sub>	Landfill leachate, Pulp and paper bleaching liquor, and Heavily organic halogen polluted industrial wastewater	SR	157–227 °C, 2–3.5 MPa of O <sub>2</sub>	[158]
Ru on AC-ceramic sphere	Resin effluent	UFBR	160–240 °C, 1.5 MPa of O <sub>2</sub>	[159]
CuO	Epoxy acrylate monomer industrial wastewater	SR	200–250 °C, 3–3.5 MPa of O <sub>2</sub>	[160]

area, a high dispersion of impregnated metal, and a narrow range of sizes [143–146]. The results suggested that the catalytic activity of Cu/ACF may be caused by the strong interaction between copper (II) oxide and ACF.

Kaewpuang-Ngam et al. [147] investigated the CWAO of ammonia over the co-precipitated transition metal (Mn, Fe, Co, Ni, and Cu)-aluminium catalysts. Among the prepared catalysts, the Cu-Al-O catalyst exhibited the highest activity and selectivity to molecular nitrogen. It was suggested that CuO promotes the reaction and CuAl<sub>2</sub>O<sub>4</sub> in bulk phase stabilizes the catalyst. Kaewpuang-Ngam et al. [148] also reported that about 90% of nitrogen selectivity for the CWAO of ammonia was achieved by using the 20 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after 2 h reaction at 230 °C and 2 MPa without the dissolution of Ni. The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst pretreated by calcination in air at 900 °C for 4 h showed a high stability due to the formation of metal aluminate, NiAl<sub>2</sub>O<sub>4</sub> phase.

#### 2.4. Catalytic wet air oxidation of industrial wastewaters

As mentioned above, heterogeneous catalysts have been extensively studied for the CWAO of various model compounds. However, few works have focused on the feasibility of solid catalysts for the treatment of real wastewater. Some of studies on the CWAO of industrial wastewaters are summarized in Table 9.

Pulp and paper industry uses very large amounts of water during the processing. Especially, the bleaching process produces refractory organic compounds including lignin and polysaccharide fragments, organic acids, aliphatic alcohols, etc., which are hardly degraded by biological treatment. Pintar et al. [149] investigated the CWAO of acidic and alkaline Kraft bleaching plant effluents (TOC = 665 and 1380 mg/L, respectively) in a batch slurry reactor. The results showed that TiO<sub>2</sub> and ZrO<sub>2</sub> were considerably active in the TOC removal of both acidic and alkaline effluents, and the rate

of TOC removal increased with the specific surface area of metal oxides. Doping of Ru on these metal oxides enhanced the catalytic activity, and thus more than 99% of TOC removal was achieved within 8 h of reaction at 190 °C and 5.5 MPa of air. The CWAO of Kraft bleach plant effluents in a trickle-bed reactor packed with Ru/TiO<sub>2</sub> demonstrated the ultimate destruction of parent organics and their mineralization to CO<sub>2</sub>, and proved the long-term activity and chemical stability of the Ru/TiO<sub>2</sub> catalyst [150]. The reaction was characterized by a fast initial step with rapid fragmentation of large molecules to short organic acids, followed by a slow reaction step as these acids, especially acetic acid, tend to be resistant to further oxidation [151]. Complete destruction of acetic acid is not necessary because acetic acid can be eliminated by biological treatment due to its low ecotoxicity. Therefore, the CWAO process can be adapted as a pretreatment process integrated with subsequent biological treatment of acetic acid to recycle the industrial effluents.

Olive oil mill wastewater (OMW) generated from olive oil extraction industry has a high organic load and antibacterial phenolic compounds and thus poses severe environmental threats. Minh et al. [152] reported that TOC and phenolic content of OMW were effectively eliminated through the CWAO using the noble metals (Pt and Ru) supported on titania and zirconia at 190 °C and 70 bar of air, in which the toxicity towards *Vibrio fischeri* and phytotoxicity decreased simultaneously. Especially, the CWAO over the Ru catalysts reduced considerably the total phenolic contents of OMW and thus produced the effluent suitable to be treated by anaerobic treatment. The Ru catalysts were found to be stable over a long period of operation in a trickle-bed reactor. Gomes et al. [153] reported that the carbon supported Pt and Ir catalysts showed a high activity for the CWAO of OMW. With the 1 wt% Pt/C catalyst, TOC and color were completely removed after 8 h of reaction at 200 °C and 6.9 bar of O<sub>2</sub>.

Coke-plant wastewater is generated from coal coking, coal gas purification, and by-product recovery processes of coke factory. Yang et al. [154] studied the CWAO of coke-plant wastewater using the eggshell Ru/TiO<sub>2</sub> catalyst with 0.25 wt% Ru loading at 250 °C and 4.8 MPa, in which COD removal and ammonia/ammonium compounds (NH<sub>3</sub>-N) removal were 96% and 93%, respectively. The eggshell Ru/TiO<sub>2</sub> catalyst showed the higher activity for COD removal and much higher activity for NH<sub>3</sub>-N degradation than the corresponding uniform Ru/TiO<sub>2</sub> catalyst due to the higher density of active Ru sites in the shell layer. Han et al. [155] investigated the CWAO of high-strength organic coking wastewater over the Ce-Cu and Ce-Mn catalysts. The Cu-Ce (2:1) catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> showed a high activity and stability. With this catalyst, a 95.2% of COD was removed after 60 min of reaction at 180 °C and 1.2 MPa of O<sub>2</sub>, while the concentration of leached copper ions was only 5.81 mg/L.

The effluent from dye and textile industry generally exhibits a deep color which prevents the transmission of light and thus adversely affects the aquatic ecosystems. Rodríguez et al. [156] demonstrated that CNF can be effectively used as a catalyst support for the CWAO of washing textile wastewater. In the presence of 3 wt% Cu/CNF catalyst, color reduction and TOC removal were close to 97% and 74.1%, respectively, after 180 min of reaction under 140 °C and 8.7 bar of oxygen pressure. The 43% of toxicity was simultaneously reduced, which was evaluated by the acute toxicity results based on bioluminescence in *Vibrio fischeri*.

Belkacemi et al. [157] conducted the CWAO of two high strength alcohol-distillery waste liquors (TOC = 10,500 and 22,500 mg/L, respectively) in a batch stirred autoclave (180–250 °C, 0.5–2.5 MPa of O<sub>2</sub>). Mn/Ce oxides and Cu(II)/NaY showed higher TOC removal than Pt/Al<sub>2</sub>O<sub>3</sub>. The initial rates were first order for TOC, and the activation energies for the three different catalysts ranged from 34 to 51 kJ/mol. Although the catalysts were found to be very effective

for short contact times, for prolonged exposures coke deposition hampered the access of dissolved compounds to the active sites, thereby drastically lowering the TOC reduction rates.

Goi et al. [158] carried out the CWAO of three high strength composite halogenated liquid wastes, i.e. landfill leachate, pulp and paper bleaching liquor, and heavily organic halogen polluted industrial wastewater, in a batch bench-top pressure vessel using pure CeO<sub>2</sub> and SiO<sub>2</sub>-doped CeO<sub>2</sub>. The SiO<sub>2</sub>-doped CeO<sub>2</sub> showed a better performance than pure ceria due to the higher OSC of silica-modified ceria coupled with high surface area. Landfill leachate and heavily organic halogen polluted industrial wastewater were more refractory than pulp and paper bleaching liquor. For the CWAO of pulp and paper bleaching liquor with the SiO<sub>2</sub>-doped CeO<sub>2</sub>, about 80% of COD and 90% of adsorbable organic halogen (AOX) were removed for 1 h reaction at 187 °C. The CWAO of heavily polluted wastewaters increased the biodegradability to a degree that allows wastewaters to be then treated in biological method.

Resin effluent (COD = 19,500 mg/L) containing phenol, formaldehyde, and methanol was treated by CWAO using the Ru catalyst on active carbon-ceramic sphere prepared by coating a porous ceramic sphere with a phenolic resin as the carbon precursor [159]. The results showed that the 3 wt% of Ru catalyst on support activated by KOH with the KOH-to-carbon ratio of 1.2 displayed the highest activity and stability during 30 days. With this catalyst, the conversion of COD was about 92% at 200 °C and 1.5 MPa of O<sub>2</sub>.

Yang et al. [160] examined the feasibility of CWAO as a pretreatment method for biological remediation through the CWAO of epoxy acrylate monomer industrial wastewater (COD = 150,000 mg/L and TOC = 53,000 mg/L). After 3 h of CWAO over the CuO catalyst at 250 °C and 3.5 MPa of O<sub>2</sub>, the 77% of COD and 54% of TOC were removed, respectively. Moreover, the BOD<sub>5</sub>/COD ratio significantly increased from 0.13 to 0.70, indicating that the biodegradability is highly improved through CWAO.

## 2.5. Integration of catalytic wet air oxidation to other processes

The combination of appropriate techniques is considered imperative to conceive technically and economically feasible wastewater treatment because a single treatment method does not appear to be efficient for a highly concentrated wastewater. In this sense, CWAO can be used more efficiently through integration with other processes. Representative hybrid systems related to CWAO are the integrated CWAO/biological process and the hydrogen promoted-CWAO.

As mentioned in Section 2.4, CWAO can effectively improve the biodegradability of industrial wastewater, and accordingly the integration of CWAO and biological process can be a cost-effective process for the treatment of non-biodegradable wastewaters [12]. CWAO as a pretreatment step converts bioresistant compounds to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass, and water. The biodegradability expressed as a BOD<sub>5</sub>/COD ratio and ecotoxicity of effluent after CWAO step is a determining factor for the potential application of this combined strategy [62,161–166]. Recently, Kang et al. [167] investigated the feasibility of coupling a CWAO using the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst and an anaerobic/aerobic biological process to treat wastewater from Vitamin B<sub>6</sub> production. The Results showed that the CWAO enhanced the biodegradability (BOD<sub>5</sub>/COD) from 0.10 to 0.80. The oxidized effluent with COD of 10,000 mg/L was subjected to subsequent continuous anaerobic/aerobic oxidation, and a 99.3% of total COD removal was achieved. Suarez-Ojeda et al. [164] also confirmed the effectiveness of coupling a CWAO using activated carbon and an aerobic biological treatment to treat a high-strength o-cresol wastewater in a pilot scale.

The use of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as a free radical promoter in CWAO has been shown to enhance the rate of organic oxidation and eliminate the induction period [168–171]. Quintanilla et al. [171] studied the effect of hydrogen peroxide on the CWAO of phenol with activated carbon catalysts. They demonstrated that hydroperoxy radicals produced by the reaction between hydrogen peroxide and adsorbed oxygen initiate the reaction on the carbon and in the liquid phase, and are responsible for the increased initial activity which provokes a faster removal of organics.

It is necessary to exert continuous efforts on development of effective hybrid systems using CWAO as a pretreatment as well as a posttreatment depending on the nature of wastewater from various industries.

### 3. Reaction mechanisms and kinetics for catalytic wet air oxidation

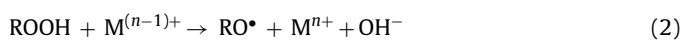
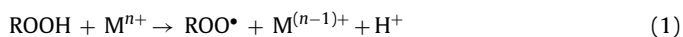
The majority of studies for CWAO mainly focus on the removal of reactant, COD, and TOC. However, a sufficient knowledge for reaction mechanisms and kinetics for CWAO is essential to optimize the reaction conditions and to develop the effective catalysts required for industrial applications.

#### 3.1. Reaction mechanisms and pathways

The definite mechanisms and reaction pathways for CWAO have not been established even for a pure compound because the oxidation of organic compounds goes through very complicated routes and leads to the formation of various intermediates [172,173]. Generally, the final intermediates are short-chain organic acids such as acetic acid, formic acid, oxalic acid, etc., regardless of initial organic compounds [174,175]. The identification of intermediates and by-products formed during oxidation is essential to evaluate the toxicity and to point out possible refractory compounds.

Before discussing about CWAO, it is necessary to consider the uncatalyzed WAO because its mechanisms are usually very similar to those for CWAO as acetic acid is also identified as a final product, besides carbon dioxide [13]. Most of studies have reported that the chemical reaction of WAO chiefly proceeds via free radical reactions. Several free radical reactions consisting of initiation, propagation, and termination of free radical have been proposed to take place during the WAO of various organic compounds [16,176–179]. Robert et al. [179] provided the direct experimental evidence for the presence of free radical intermediates in the WAO of cellulose using electron spin resonance (ESR) spectroscopy coupled with spin trapping technique. Some studies gave the indirect evidences of free radical reactions. Co-oxidation is one of them, which involves the oxidation of an organic compound by free radical intermediates generated from another organic compound [180–183]. Another is to hinder or promote the free radical reactions using inhibitors such as *t*-butanol [184,185] or promoters like hydrogen peroxide and hydroquinone [184,186], respectively.

Heterogeneous catalysts are capable of initiating free radicals. The catalyst directly activates reactant molecules, facilitating their decomposition into radicals, or accelerates the decomposition into radicals with hydroperoxides formed in a radical chain mechanism. The catalytic cycle can be introduced through the following reduction-oxidation reactions of hydroperoxides [187]:



The solid catalysts enhance the free radical propagation through the formation of alkyl peroxy radicals (1) and the decomposition of hydroperoxides (2). The redox potential of the  $\text{M}^{n+}/\text{M}^{(n-1)+}$  couple is a main factor to promote the oxidation. The cata-

lysts may also involve an oxygen-transfer mechanism in which the role of catalyst is to transfer an oxygen atom to aqueous reactant molecules through complexation and activation [188]. The CWAO of organic compounds may initiate by the activation of either oxygen molecules or reactant molecules. Either an adsorbed oxygen on catalyst surface or a lattice oxygen present in metal oxides may participate in a reaction [189]. Thus, the solid catalysts enhance the heterolytic reactions by the formation of ionic environment. Both free radical (homolytic) and ionic (heterolytic) oxidation reaction mechanisms have been proposed for the CWAO of organic compounds [190–194]. Sadana and Katzer [190] proposed a heterogeneous-homogeneous free radical mechanism consisting of the initiation on catalyst surface, homogeneous propagation, and either homogeneous or heterogeneous termination. Pintar and Levec [191,192] demonstrated that the CWAO of phenolic compounds combined a redox and a heterogeneous non-branched chain free radical mechanism in which the role of catalyst was ascribed to be in the activation of phenol molecule and oxygen. The critical catalyst concentration phenomenon is one of the characteristics of free radical chain reaction, in which a slight increase in catalyst concentration induces a dramatic change in the rate of process [193]. Another is an induction period where the generation of radicals is poor, followed by a higher steady-state period with a fast free radical reaction regime [194].

The CWAO of organic pollutants may involve several reaction mechanisms depending on the reaction conditions. It is also possible for one mechanism to be dominant. For the catalyst with poor activity, the free radical mechanism may predominate, and thus high catalyst concentration could lead to a longer induction period or lower oxidation rate due to the chain termination caused by interaction between free radical and catalyst. This might explain the lower pollutant conversion over some catalysts than uncatalyzed oxidation. On the other hand, the redox mechanism may predominate in the presence of catalysts with high activity.

Most of studies on reaction pathway for CWAO have employed phenol as a model compound because it is considered to be an intermediate in the oxidation of higher molecular weight aromatic compounds [22,23]. Phenol oxidation follows an extremely complex pathway composed with parallel and consecutive reactions. Devlin and Harris [195] proposed the mechanism for non-catalytic oxidation of phenol in which phenol is firstly oxidized to dihydroxybenzenes, i.e. hydroquinone and catechol, which are converted into benzoquinones. Rings of benzoquinones are then opened with the formation of appropriate acids which are further oxidized to short-chain carboxylic acids. Among the generated carboxylic acid, acetic acid is considered as the most refractory compound due to a low adsorption coefficient on catalyst surface and/or a weak reactivity in adsorbed state [196]. Acetic acid is not important from an environmental point of view because it is readily biodegradable. However, it causes pH values as low as 3, thus requiring reactor materials and catalysts that can withstand the hot and corrosive reaction conditions.

As depicted in Fig. 1, most of studies on the oxidation routes for the CWAO of phenol generally consider the hydroxylation of phenol to hydroquinone and catechol as a first step with a further oxidation of them to benzoquinones [70,174,175,197,198]. However, many different intermediates are evidently formed during CWAO, depending on catalysts and reaction conditions such as temperature, oxygen pressure, and solution pH. Santos et al. [199,200] investigated the effect of solution pH on the reaction pathway for the CWAO of phenol by using bicarbonate as a buffer reagent to maintain the pH in the range of 7–8 (designated as pH 8B). The experimental results showed that the toxic intermediates such as hydroquinone, benzoquinone, and catechol were not obtained at pH 8B, while they were found in the catalytic phenol oxidation at acidic pH of 3.5 [175]. The intermediates detected at pH 8B were

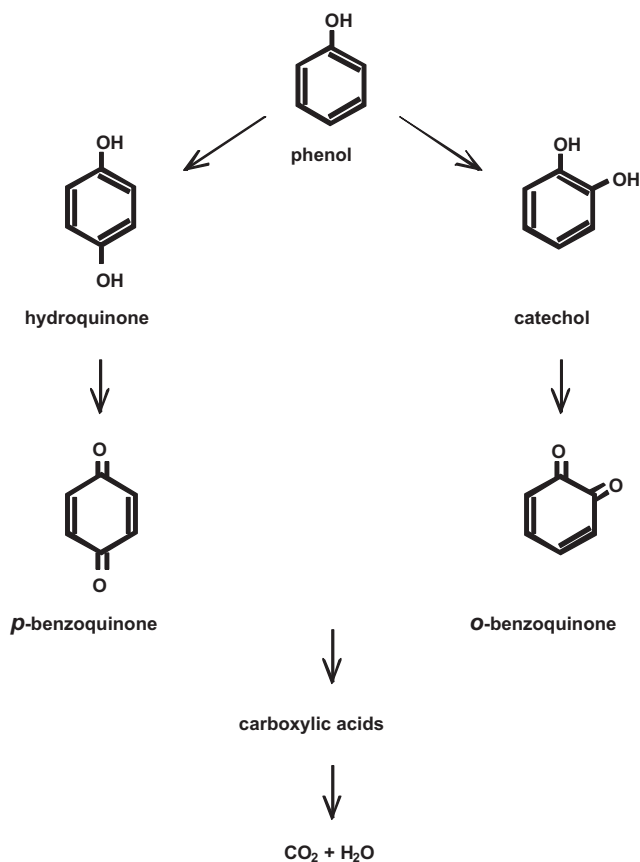


Fig. 1. Simplified reaction pathway of phenol oxidation.

more than one order of magnitude less toxic than phenol [163]. A radical mechanism was proposed to explain this oxidation route, in which bicarbonate reacts with phenoxy radicals formed on the solid surface, avoiding the formation of hydroperoxide radical precursors of dihydroxybenzenes.

### 3.2. Reaction kinetics

It is desired that the kinetic models correspond reasonably with reaction mechanism and experimental data. Reaction parameters including reaction temperature, oxygen partial pressure, reactant concentration, solution pH, reactor type, etc. influence the reaction rate. Studies on the kinetics of CWAO have been extensively performed by using model compounds over a wide range of temperatures and pressures. Slurry reactors and fixed-bed reactors (both liquid full-operating and trickle-bed) are mainly used to carry out the CWAO runs. The solid-to-liquid volumetric ratio, usually called catalyst concentration, is quite low in slurry reactors (about 1–5 g/L) and several orders higher in fixed-bed reactors.

For the heterogeneous catalytic oxidation of aqueous organic pollutants, the apparent kinetic models are generally expressed in terms of either the simple power law or more complex equation based on adsorption–desorption mechanism, i.e. Langmuir–Hinshelwood–Hougen–Watson (LHHW) model. Both kinetic models have provided reasonable simulations of the observed results for the CWAO of reactants [23,84,174,201–206]. Kinetic models proposed from data obtained in slurry reactors are usually power law type with different orders for reactant concentration, oxygen partial pressure, and catalyst concentration, with the exponent of the last variable being less than unity due to homogeneous contribution. On the other hand, kinetic models proposed from data obtained in fixed-bed reactors only consider heteroge-

**Table 10**  
Kinetic models proposed for heterogeneous CWAO [207].

Kinetic model	Equation	Mechanism
M1	$r_H = k_1 [A]^p [O_2]^q$	Empirical approach
M2	$r_H = \frac{k_1 K_A K_{O_2} [A] [O_2]}{(1 + K_A [A] + K_{O_2} [O_2])^2}$	Single site; $O_2 + * \leftrightarrow O_2^*$
M3	$r_H = \frac{k_1 K_A K_{O_2}^{0.5} [A] [O_2]^{0.5}}{(1 + K_A [A] + K_{O_2}^{0.5} [O_2]^{0.5})^2}$	Single site; $O_2 + 2^* \leftrightarrow 2O_2^*$
M4	$r_H = \frac{k_1 K_A K_{O_2}^{0.5} [A] [O_2]^{0.5}}{(1 + K_A [A])(1 + K_{O_2}^{0.5} [O_2]^{0.5})}$	Dual site; $O_2 + 2^* \leftrightarrow 2O_2^*$

neous contribution with the rate of pollutant degradation, being linear with catalyst concentration.

The CWAO of organic compounds consists of the following steps occurring in series: the dissolution of oxygen from bulk gas phase to bulk liquid phase, the competitive or parallel adsorptions of the dissolved oxygen and reactant on the active sites of catalyst, and the surface chemical reactions. Guo and Al-Dahhan [207] suggested the kinetic equations for heterogeneous contribution,  $r_H$ , based on the reaction mechanism where the adsorption and desorption steps are assumed to be instantaneous compared to the surface reaction (Table 10). The simplest form of surface reaction rate could be correlated with the power law kinetic model M1. The LHHW rate laws are commonly used to express heterogeneous catalytic kinetics due to a more realistic description of reaction mechanism [208–210]. On the basis of the LHHW rate laws, model M2 consists of reversible adsorption of reactant and oxygen molecules on the same active site of catalyst, and a rate-determining irreversible surface reaction between the adsorbed reactant and adsorbed oxygen. Model M3 is very similar to model M2 in terms of its single-site mechanism except the dissociation of oxygen molecules to oxygen atoms. On the other hand, if the dissociated oxygen and reactant adsorb on distinctly different active sites, the surface reaction rate is described as model M4. In all rate expressions,  $k_1$  is the rate constant for the surface reaction step, which can be expressed by the Arrhenius law, and  $K_A$  and  $K_{O_2}$  are the adsorption equilibrium constants for model compound and oxygen on the catalyst surface, respectively. Guo and Al-Dahhan [207] evaluated a group of kinetic models considering both power law and LHHW approaches to describe the kinetics for the CWAO of phenol over the extrudates of Al-Fe pillared clay in a basket stirred-tank reactor. The results showed that the apparent catalytic kinetics of phenol disappearance complied with a LHHW rate law derived from a dual site adsorption mechanism with a rate-determining surface reaction between adsorbed phenol and adsorbed oxygen atoms. Gunale and Mahajani [211] reported that the kinetic data for the CWAO of N-ethylethanolamine over Ru/TiO<sub>2</sub> could be well correlated by a LHHW model involving a dual site dissociative adsorption of O<sub>2</sub>.

Fortuny et al. [201] carried out the CWAO of phenol under 120–160 °C and 0.6–1.2 MPa of O<sub>2</sub> using a commercial copper oxide catalyst (Harshaw Cu 0803 T1/8, Engelhard) in a trickle-bed reactor. They described the phenol degradation using a simple power law expression in which reaction order for phenol and oxygen were 1 and 0.5, respectively. In their successive work, the same experimental data was described using a LHHW expression accounting for the adsorption effects together with simple power law expression [174]. The model predictions significantly improved when LHHW expressions were incorporated for all intermediate compounds, except for phenol that did not adsorb on the catalyst. Eftaxias et al. [206] reported that simple power law model accurately predicted the entire experimental data for the CWAO of phenol using AC in a trickle-bed reactor, while more complex LHHW model did not significantly improve the data fitting. They also demonstrated that compared to a gradient-based Levenberg–Marquadt algorithm, the stochastic simulated annealing algorithm effectively optimized the

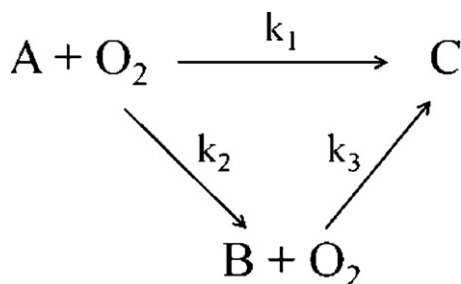


Fig. 2. Generalized lumped kinetic model (GLKM) [212].

involved model parameters, leading to a very satisfactory fit of whole experiment data [84].

Although the kinetic models proposed for pure compounds are useful for the understanding of reaction mechanisms, they are not sufficient for real wastewaters containing a mixture of organic compounds. More detailed kinetic models are required to describe the reaction rate observed in the CWAQ of real wastewaters. Therefore, the rate laws have to be expressed by means of lumped parameters such as TOC and COD. For non-catalytic WAO, Li et al. [212] proposed the general lumped kinetic model (GLKM), also named the triangular scheme, based on the simplified reaction scheme with acetic acid as a rate-limiting intermediate (Fig. 2). In the GLKM, all the organics are divided into three characteristic lumps, namely parent compounds and unstable intermediates except acetic acid (lump A), refractory intermediates, acetic acid being a typical representative (lump B), and end products (lump C).  $k_1$ ,  $k_2$ , and  $k_3$  are apparent constants for the chemical reaction rates and are dependent on reaction temperature and dissolved oxygen concentration. The GLKM has been used to analyze the experimental kinetic data in several studies [151,174,213]. Unfortunately, the GLKM does not successfully express the heterogeneous CWAQ because it does not consider the heterogeneous catalytic reaction, namely reactant and/or product adsorption/desorption as well as surface reactions. Belkacemi et al. [214] proposed the extended lumped kinetic model (ELKM) based on the LHHW expression (Fig. 3). They extended the GLKM to the heterogeneous CWAQ by including additional physical and chemical steps as follows: the parent aqueous compounds (lump A) adsorb on the catalyst surface, undergo surface reactions into adsorbed intermediate (lump B), then into end product (lump C); both may desorb and leave from the catalyst surface. The versatility of ELKM was demonstrated using literature data obtained under various experimental conditions. The lumped kinetic model based on the LHHW expression including the formation of coke deposits was also suggested by Hamoudi et al. [215].

#### 4. Catalyst deactivation in catalytic wet air oxidation

One of the major limitations in application of solid catalysts is the relatively rapid deactivation in reaction conditions of CWAQ. Heterogeneous catalysts are deactivated in CWAQ mainly due to poisoning, coke deposition, and metal leaching. Metal oxide catalysts are usually vulnerable to metal leaching in acidic condition. In

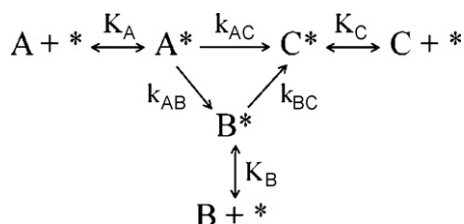


Fig. 3. Extended lumped kinetic model (ELKM) [214].

contrast, the precious metals supported on stable supports are less prone to leaching of active ingredients, but coke deposition is still a problem.

##### 4.1. Carbonaceous deposits

The major cause of catalyst deactivation in the heterogeneous CWAQ of organic compounds is the carbonaceous deposits on catalyst surface, which limit the access of reactant and dissolved oxygen to the active sites of catalyst. In the CWAQ process, the degradation of pollutants takes place preferably at moderate temperatures and pressures. Although less severe reaction conditions are economically advantageous, low temperatures promote stronger adsorptive interactions on catalyst surface, and accordingly facilitate the formation of undesirable heavy polymeric products [198,216]. Pintar et al. [24] reported that the deactivation of Ru/TiO<sub>2</sub> catalysts observed at temperatures below 190 °C was attributed to the strong adsorption of partially oxidized intermediates on catalyst surface, which can be avoided by conducting the CWAQ at sufficiently high temperatures. In a slurry reactor, the homogeneous polymerization is promoted in the bulk liquid-phase due to a low solid-to-liquid volumetric ratio [217,218]. On the other hand, the formation of polymers is usually suppressed in a fixed-bed reactor with a high solid-to-liquid ratio [191,192].

As mentioned in the Section 2, the coke deposits concern both noble metals and metal oxides. Kim et al. [37] demonstrated that the 64% of degraded phenol over MnO<sub>x</sub>/Ce<sub>0.65</sub>Zr<sub>0.35</sub>O<sub>2</sub> was converted into coke deposits during the CWAQ of phenol in a batch reactor. Kim and Ihm [34] also reported that among the transition metal (Mn, Fe, Co, Ni, and Cu) oxide catalysts on γ-Al<sub>2</sub>O<sub>3</sub>, the Mn catalyst showed the highest amount of carbonaceous deposits after the CWAQ of phenol in a batch reactor. The results of NMR and FTIR spectroscopy showed that the carbonaceous deposits were mostly of aromatic nature and contained some oxygen-bearing groups such as carboxylic acids and alcohols. Keav et al. [219] identified that the carbonaceous deposits formed during the CWAQ of phenol consist of several polycyclic aromatic compounds of chromenone, xanthenone, and fluorenone families, resulting from the condensation of phenol with partial oxidation products.

Lee et al. [220] studied the formation/migration of carbon deposits during the CWAQ of phenol over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>. They suggested that the carbonaceous deposits were primarily formed on Pt particles and then migrated continuously onto the supports. Mikulová et al. [99] suggested that the presence of carbonate species in the lattice of ceria-based support formed during the CWAQ of acetic acid was responsible for the deactivation related to an inhibition of oxygen transfer. Nouisir [33] reported the poisoning of Pt/CeO<sub>2</sub> catalysts during the CWAQ of phenol in a stirred batch reactor due to the formation of carbonates and polymeric carbon species. They showed that the introduction of zirconium into ceria lattice restrained the formation of carbonaceous materials.

Several methods have been used to regenerate the solid catalysts deactivated by coke deposition. Thermal treatment in an oxidizing gas stream is the most common regeneration method. Usually, the coke-deposited catalysts can recover their initial activity after regeneration at 400 °C under air stream [29]. A rinse with organic solvent like acetone also can be utilized to remove the coke deposits on catalyst surface [53]. Keav et al. [221] proposed an easy-to-perform ex-situ solvent-free reactivation procedure, in which the carbonaceous deposits are totally degraded by combustion with diluted oxygen at moderate temperature.

##### 4.2. Metal leaching

During the CWAQ of organic compounds, the acidic intermediates such as short-chain carboxylic acids are formed, and

accordingly the pH value of medium decreases as oxidation proceeds [222–225]. Obviously, metal ions are leached out from active species and/or supports to reactant solution under hot acidic condition, resulting in the decrease of catalytic activity [226]. Moreover, the leached metal ions usually exhibit toxicity so that a treatment is required to recover them [175,200].

Especially, the copper catalysts are very vulnerable to leaching in the CWAO conditions in spite of their good catalytic activity [35,37,38,200,222,227–229]. The rate of copper leaching considerably increases under the pH value of less than 4 [229]. Santos et al. [200] found that considerable copper leaching occurred at acid pH of 3.5, while this was negligible in the presence of bicarbonate buffer solution because the solution pH was maintained in the range of 7–8. However, the oxidation rate in the basic condition is generally lower than that in acidic condition [228]. The dissolved copper ions from the catalyst produce an important reaction extension in the liquid phase, changing the heterogeneous catalysis into the homogeneous reaction, and accordingly influence on the oxidation rate of organic compounds and the oxidation routes [38,200]. Arena et al. [38] revealed that the length of induction period in the CWAO of phenol is actually related to the leaching of a certain amount of copper ions from the catalyst. During this time, the phenol conversion and extent of copper leaching remained very low levels, while the initial pH value hardly changed. Thereafter, the extent of copper leaching rapidly increased corresponding to the drop in the pH value caused by acidic intermediates. Both phenol and TOC conversion also increased with copper leaching. The parallel evolution of Cu leaching and phenol conversion definitely proved a direct relationship between leaching and activity of the Cu catalysts. This result leads to infer that the CWAO of organic compounds over the Cu catalysts proceeds via a homogeneous-heterogeneous path promoted by leached copper ions.

#### 4.3. Mitigation of catalyst deactivation

Many attempts have been made to avoid or reduce the carbonaceous deposits and/or metal leaching through the modification of catalyst composition, the introduction of promoter, the development of manufacturing method and pretreatment procedure, and the control of operating conditions.

Hamoudi et al. [230] reported that even though the MnO<sub>2</sub>-CeO<sub>2</sub> catalyst was very effective for the degradation of phenol, the mineralization selectivity was moderate due to the parallel formation of carbonaceous deposits. Promotion of the MnO<sub>2</sub>-CeO<sub>2</sub> catalyst with Pt and/or Ag appreciably reduced the amount of coke deposits due to the low temperature redox properties attained by metal doping, and accordingly enhanced the mineralization selectivity.

Hussain et al. [231,232] ascertained that doping of potassium enhanced the catalytic activity of Mn-Ce-O catalyst for the CWAO of phenol and decreased the formation of carbonaceous deposits. Thus, mineralization selectivity of the K-Mn-Ce-O catalyst was 2.9 times higher than that of Mn-Ce-O. Furthermore, the K-Mn-Ce-O catalyst exhibited a high resistance to metal leaching. Potassium having electron-donor ability captures oxygen atoms, and accordingly forms K<sub>2</sub>O which subsequently changes to peroxide, O<sub>2</sub><sup>-</sup>, generating an electron rich environment that is favorable to the activation of oxygen. This in turn contributes to the production of more peroxide by catalyst. Thus, the oxidation occurs more rapidly with a high efficiency, thereby reducing the formation of coke deposits [233].

To minimize the metal leaching, the polytetrafluorethylene (PTFE) coated catalyst was proposed [234]. The presence of hydrophobic film would reduce the direct contact between active species and aqueous reaction medium, and allow the reactants to diffuse and react into the catalyst. An optimized wet-proofed catalyst was prepared by successive immersion steps of a conven-

tional CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in a PTFE fibers suspension. The activity of wet-proofed catalyst was remained almost constant, while the activity of conventional catalyst decreased with reaction time. The hydrophobic layer improved catalyst stability by preventing the solubilization of Cu<sup>2+</sup> and the formation of boehmite phase during reaction [235].

Spinel type catalysts are highly resistant to dissolution in acidic conditions [236,237]. Xu et al. [238] reported that when  $x \leq 0.25$  for the Cu<sub>0.5-x</sub>Fe<sub>x</sub>Zn<sub>0.5</sub>Al<sub>2</sub>O<sub>4</sub> spinel catalysts, the amount of Cu leaching decreased during the CWAO of phenol due to the reduction in the fraction of octahedral Cu exposed to reactants. They also showed that increasing with Al content in the ZnFe<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub> spinel catalysts, the main iron species present on catalyst surface turned from aggregated iron oxide clusters to Fe<sup>3+</sup> species in octahedral sites which are very resistant to dissolution under acidic condition [239,240].

## 5. Conclusions

Catalytic wet air oxidation is a promising technology for the treatment of refractory organic pollutants in the effluent from various industries in view of high pollutant removal efficiency at mild conditions and environmental friendliness not involving any harmful chemical reagent. Studies on the CWAO of model pollutants and industrial effluents illustrate the potential of CWAO as a treatment technology for industrial wastewater. Most of studies have usually employed phenolics, carboxylic acids, and nitrogen-containing compounds as a model pollutant. Among them, phenol is mainly taken as a model compound because it is widely used in industries and is considered to be an intermediate in the oxidation of higher molecular weight aromatic compounds.

The performances of various solid catalysts including noble metals such as Ru, Rh, Pd, Ir, and Pt as well as oxides of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ce for the CWAO of aqueous pollutants have been demonstrated in the last decade. The results evidently showed that catalytic activity and stability depend on the combination of metal and support, the preparation and pretreatment method, the nature of pollutants, and the reaction conditions. Noble metals have been extensively utilized in the CWAO of model compounds as well as real wastewaters due to their excellent catalytic activities. Although noble metals show a high resistance to dissolution, they are still vulnerable to poisons including polymeric product formed during CWAO. Among the base metal oxide catalysts, copper oxide catalysts exhibit a high activity for the CWAO of organic compounds, especially phenol. However, they are vulnerable to metal leaching under hot acidic conditions caused by acidic intermediates, i.e. short-chain carboxylic acids. Mixed metal oxides such as CeO<sub>2</sub>-ZrO<sub>2</sub>, CeO<sub>2</sub>-TiO<sub>2</sub>, CuCeO<sub>x</sub>, and MnCeO<sub>x</sub> are more promising for the CWAO of organic pollutants in terms of catalytic activity and resistance to metal leaching.

Some metal oxides such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, etc. have been mainly used as supporting materials. Among them, ceria-based materials are one of the most promising supports due to their redox and morphological properties promoting the production of active radicals or direct redox reaction. Carbon materials including activated carbon, graphite, carbon nanotubes, etc. are also prospective materials as a support in view of high adsorption capacity and good stability in various reaction media.

During the CWAO of organic compounds, heterogeneous catalysts are deactivated mainly by carbonaceous deposits and metal leaching. Coke deposition on the catalyst surface quickly deactivates the catalysts by blocking the active sites. More polymeric deposits are formed in the bulk liquid phase in slurry reactors, mainly used for the lab-scale CWAO experiments, due to a low solid-to-liquid volumetric ratio. On the other hand, the formation

of polymeric products can be suppressed in fixed-bed reactors in which a solid-to-liquid ratio is high. It was found that the introduction of promoter, especially potassium, to Mn-Ce-O catalysts drastically reduced the amount of carbonaceous deposits. Metal ions are leached out from catalysts to reactant solution under hot acidic condition, resulting in the decrease of catalytic activity. Moreover, the leached metal ions can cause environmental harm due to their toxicity. It was demonstrated that metal leaching was effectively inhibited by the adjustment of solution pH to basic condition using bicarbonate and by the coating of hydrophobic film using polytetrafluoroethylene (PTFE).

Generally, the complete oxidation of organic pollutants to carbon dioxide and water is hard to achieve due to the formation of more refractory intermediates like short-chain carboxylic acids. CWAO integrated with biological process can be more attractive for the treatment of industrial wastewater containing toxic pollutants because short-chain carboxylic acids, especially acetic acid, are readily biodegradable due to their low ecotoxicity. Biodegradability and toxicity of the treated effluent from CWAO should be checked to evaluate the suitability for the subsequent biological process.

Further studies are necessary to develop more active and stable catalysts which can be effectively utilized on industrial scale. Base metal oxide catalysts are more desirable than noble metals in terms of cost and resistance to poisoning by halogen-containing substance, though their activities are still lower than noble metals. Among them, Cu, Mn, and Ce are the most prospective species to compete with noble metals. Although the supporting materials having high surface area render a better dispersion of active species resulting in higher catalytic activity, the deactivation related to metal leaching and carbonaceous deposits are still remained. Insertion of active species into the lattice structure, e.g. mixed metal oxides, and the addition of promoter can reduce significantly the amount of metal leaching and coke deposits, respectively. Carbon materials, especially activated carbon, is also a promising catalyst avoiding the leaching problem and become more effective through a pretreatment introducing surface functional groups. It is interesting to note the type of catalyst, especially polyoxometalates, showing a good activity under room conditions. Preparation method can control the chemical (oxidation state) and physical properties of catalyst by controlling the stoichiometric ratio and the size/geometry of active components, thereby influencing catalytic activity and stability. Catalytic performance can be improved significantly by modifying the conventional preparation methods like incipient wetness impregnation, precipitation, sol-gel method, etc. It is desired to make a thorough investigation on reaction mechanisms and kinetics which provides important information for industrial applications.

## Acknowledgement

This work was supported by Eco-technopia 21 Project, Brain Korea 21 Project, and also by National Research Laboratory Project.

## References

- [1] H. Debellefontaine, M. Chakchouk, J.N. Foussard, D. Tissot, P. Striolo, Treatment of organic aqueous wastes: wet air oxidation and wet peroxide oxidation(R), *Environ. Pollut.* 92 (1996) 155–164.
- [2] T.G. Danis, T.A. Albanis, D.E. Petrakis, P.J. Pomonis, Removal of chlorinated phenols from aqueous solutions by adsorption on alumina pillared clays and mesoporous alumina aluminum phosphates, *Water Res.* 32 (1998) 295–302.
- [3] W.H. Glaze, J.W. Kang, D.H. Chapin, The chemistry of water-treatment processes involving ozone, hydrogen-peroxide and ultraviolet-radiation, *Ozone-Sci. Eng.* 9 (1987) 335–352.
- [4] F.J. Zimmermann, New waste disposal process, *Chem. Eng.* 65 (1958) 117–120.
- [5] F.E. Hancock, Catalytic strategies for industrial water re-use, *Catal. Today* 53 (1999) 3–9.
- [6] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation, *Ind. Eng. Chem. Res.* 34 (1995) 2–48.
- [7] F. Luck, A review of industrial catalytic wet air oxidation processes, *Catal. Today* 27 (1996) 195–202.
- [8] Y.I. Matatov-Meytal, M. Sheintuch, Catalytic abatement of water pollutants, *Ind. Eng. Chem. Res.* 37 (1998) 309–326.
- [9] S. Imamura, Catalytic and noncatalytic wet oxidation, *Ind. Eng. Chem. Res.* 38 (1999) 1743–1753.
- [10] S.T. Kolaczowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Wet air oxidation: a review of process technologies and aspects in reactor design, *Chem. Eng. J.* 73 (1999) 143–160.
- [11] F. Luck, Wet air oxidation: past, present and future, *Catal. Today* 53 (1999) 81–91.
- [12] D. Mantzavinos, M. Sahibzada, A.G. Livingston, I.S. Metcalfe, K. Hellgardt, Wastewater treatment: wet air oxidation as a precursor to biological treatment, *Catal. Today* 53 (1999) 93–106.
- [13] H. Debellefontaine, J.N. Foussard, Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe, *Waste Manage.* 20 (2000) 15–25.
- [14] L. Oliviero, J. Barbier, D. Duprez, Wet air oxidation of nitrogen-containing organic compounds and ammonia in aqueous media, *Appl. Catal. B: Environ.* 40 (2003) 163–184.
- [15] F. Larachi, Catalytic wet oxidation: micro-meso-macro methodology from catalyst synthesis to reactor design, *Top. Catal.* 33 (2005) 109–134.
- [16] S.K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, *Ind. Eng. Chem. Res.* 45 (2006) 1221–1258.
- [17] A. Cybulski, Catalytic wet air oxidation: are monolithic catalysts and reactors feasible? *Ind. Eng. Chem. Res.* 46 (2007) 4007–4033.
- [18] J. Levec, A. Pintar, Catalytic wet-air oxidation processes: a review, *Catal. Today* 124 (2007) 172–184.
- [19] J. Levec, Wet oxidation processes for treating industrial wastewaters, *Chem. Biochem. Eng. Q* 11 (1997) 47–58.
- [20] B.B. Pruden, H. Le, Wet air oxidation of soluble components in waste-water, *Can. J. Chem. Eng.* 54 (1976) 319–325.
- [21] S.S.Y. Lin, D.J. Chang, C.H. Wang, C.C. Chen, Catalytic wet air oxidation of phenol by CeO<sub>2</sub> catalyst—effect of reaction conditions, *Water Res.* 37 (2003) 793–800.
- [22] Z.Y. Ding, S. Aki, M.A. Abraham, Catalytic supercritical water oxidation: phenol conversion and product selectivity, *Environ. Sci. Technol.* 29 (1995) 2748–2753.
- [23] A. Santos, P. Yustos, B. Durban, F. Garcia-Ochoa, Catalytic wet oxidation of phenol: kinetics of the mineralization rate, *Ind. Eng. Chem. Res.* 40 (2001) 2773–2781.
- [24] A. Pintar, J. Batista, T. Tisler, Catalytic wet-air oxidation of aqueous solutions of formic acid, acetic acid and phenol in a continuous-flow trickle-bed reactor over Ru/TiO<sub>2</sub> catalysts, *Appl. Catal. B: Environ.* 84 (2008) 30–41.
- [25] E. Castillejos-Lopez, A. Maroto-Valiente, D.M. Nevskaia, V. Munoz, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Comparative study of support effects in ruthenium catalysts applied for wet air oxidation of aromatic compounds, *Catal. Today* 143 (2009) 355–363.
- [26] J. Barbier, L. Oliviero, B. Renard, D. Duprez, Role of ceria-supported noble metal catalysts (Ru, Pd, Pt) in wet air oxidation of nitrogen and oxygen containing compounds, *Top. Catal.* 33 (2005) 77–86.
- [27] J.B. Wang, W.P. Zhu, S.X. Yang, W. Wang, Y.R. Zhou, Catalytic wet air oxidation of phenol with pelletized ruthenium catalysts, *Appl. Catal. B: Environ.* 78 (2008) 30–37.
- [28] L. Oliviero, J. Barbier, D. Duprez, A. Guerrero-Ruiz, B. Bachiller-Baeza, I. Rodriguez-Ramos, Catalytic wet air oxidation of phenol and acrylic acid over Ru/C and Ru-CeO<sub>2</sub>/C catalysts, *Appl. Catal. B: Environ.* 25 (2000) 267–275.
- [29] P. Massa, F. Ivorra, P. Haure, F.M. Cabello, R. Fenoglio, Catalytic wet air oxidation of phenol aqueous solutions by 1% Ru/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by different methods, *Catal. Commun.* 8 (2007) 424–428.
- [30] Z.P.G. Masende, B.F.M. Kuster, K.J. Ptasinski, F. Janssen, J.H.Y. Katima, J.C. Schouten, Support and dispersion effects on activity of platinum catalysts during wet oxidation of organic wastes, *Top. Catal.* 33 (2005) 87–99.
- [31] C.D. Taboada, J. Batista, A. Pintar, J. Levec, Preparation, characterization and catalytic properties of carbon nanofiber-supported Pt, Pd, Ru monometallic particles in aqueous-phase reactions, *Appl. Catal. B: Environ.* 89 (2009) 375–382.
- [32] S.K. Kim, S.K. Ihm, Effects of Ce addition and Pt precursor on the activity of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for wet oxidation of phenol, *Ind. Eng. Chem. Res.* 41 (2002) 1967–1972.
- [33] S. Nouisir, S. Keav, J. Barbier, M. Bensitel, R. Brahmi, D. Duprez, Deactivation phenomena during catalytic wet air oxidation (CWAO) of phenol over platinum catalysts supported on ceria and ceria-zirconia mixed oxides, *Appl. Catal. B: Environ.* 84 (2008) 723–731.
- [34] S.K. Kim, S.K. Ihm, Nature of carbonaceous deposits on the alumina supported transition metal oxide catalysts in the wet air oxidation of phenol, *Top. Catal.* 33 (2005) 171–179.
- [35] S.K. Kim, K.H. Kim, S.K. Ihm, The characteristics of wet air oxidation of phenol over CuO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts: effect of copper loading, *Chemosphere* 68 (2007) 287–292.
- [36] J.R. Kim, W.J. Myeong, S.K. Ihm, Characteristics in oxygen storage capacity of ceria-zirconia mixed oxides prepared by continuous hydrothermal synthesis in supercritical water, *Appl. Catal. B: Environ.* 71 (2007) 57–63.

- [37] K.H. Kim, J.R. Kim, S.K. Ihm, Wet oxidation of phenol over transition metal oxide catalysts supported on  $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$  prepared by continuous hydrothermal synthesis in supercritical water, *J. Hazard. Mater.* 167 (2009) 1158–1162.
- [38] F. Arena, R. Giovenco, T. Torre, A. Venuto, A. Parmaliana, Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol, *Appl. Catal. B: Environ.* 45 (2003) 51–62.
- [39] S. Hocevar, U.O. Krasovec, B. Orel, A.S. Arico, H. Kim, CWO of phenol on two differently prepared CuO-CeO<sub>2</sub> catalysts, *Appl. Catal. B: Environ.* 28 (2000) 113–125.
- [40] Q. Wu, X. Hu, P.L. Yue, X.S. Zhao, G.Q. Lu, Copper/MCM-41 as catalyst for the wet oxidation of phenol, *Appl. Catal. B: Environ.* 32 (2001) 151–156.
- [41] C. Deleitenburg, D. Goi, A. Primavera, A. Trovarelli, G. Dolcetti, Wet oxidation of acetic acid catalyzed by doped ceria, *Appl. Catal. B: Environ.* 11 (1996) L29–L35.
- [42] S. Imamura, Y. Okumura, T. Nishio, K. Utani, Y. Matsumura, Wet-oxidation of a model domestic wastewater on a Ru/Mn/Ce composite catalyst, *Ind. Eng. Chem. Res.* 37 (1998) 1136–1139.
- [43] J. Barbier, F. Delanoë, F. Jabouille, D. Duprez, G. Blanchard, P. Isnard, Total oxidation of acetic acid in aqueous solutions over noble metal catalysts, *J. Catal.* 177 (1998) 378–385.
- [44] A. Trovarelli, *Catalysis by Ceria and Related Materials*, Imperial College Press, London, 2002.
- [45] A. Trovarelli, Catalytic properties of ceria and CeO<sub>2</sub>-containing materials, *Catal. Rev.-Sci. Eng.* 38 (1996) 439–520.
- [46] J.I. Gutierrez-Ortiz, B. de Rivas, R. Lopez-Fonseca, J.R. Gonzalez-Velasco, Combustion of aliphatic C-2 chlorohydrocarbons over ceria-zirconia mixed oxides catalysts, *Appl. Catal. A: Gen.* 269 (2004) 147–155.
- [47] F. Zamar, A. Trovarelli, C. Deleitenburg, G. Dolcetti, CeO<sub>2</sub>-based solid-solutions with the fluorite structure as novel and effective catalysts for methane combustion, *J. Chem. Soc.-Chem. Commun.* (1995) 965–966.
- [48] C. Bozo, N. Guilhaume, E. Garbowski, M. Primet, Combustion of methane on CeO<sub>2</sub>-ZrO<sub>2</sub> based catalysts, *Catal. Today* 59 (2000) 33–45.
- [49] L. Oliviero, J. Barbier, D. Duprez, H. Wahyu, J.W. Ponton, I.S. Metcalfe, D. Mantzavinou, Wet air oxidation of aqueous solutions of maleic acid over Ru/CeO<sub>2</sub> catalysts, *Appl. Catal. B: Environ.* 35 (2001) 1–12.
- [50] S.S. Lin, C.L. Chen, D.J. Chang, C.C. Chen, Catalytic wet air oxidation of phenol by various CeO<sub>2</sub> catalysts, *Water Res.* 36 (2002) 3009–3014.
- [51] I.P. Chen, S.S. Lin, C.H. Wang, L. Chang, J.S. Chang, Preparing and characterizing an optimal supported ceria catalyst for the catalytic wet air oxidation of phenol, *Appl. Catal. B: Environ.* 50 (2004) 49–58.
- [52] L.Z. Chang, I.P. Chen, S.S. Lin, An assessment of the suitable operating conditions for the CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyzed wet air oxidation of phenol, *Chemosphere* 58 (2005) 485–492.
- [53] I.P. Chen, S.S. Lin, C.H. Wang, S.H. Chang, CWAO of phenol using CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> with promoter—effectiveness of promoter addition and catalyst regeneration, *Chemosphere* 66 (2007) 172–178.
- [54] H. Chen, A. Sayari, A. Adnot, F. Larachi, Composition-activity effects of Mn-Ce-O composites on phenol catalytic wet oxidation, *Appl. Catal. B: Environ.* 32 (2001) 195–204.
- [55] A.F.J. Santiago, J.F. Sousa, R.C. Guedes, C.E.M. Jeronimo, M. Benachour, Kinetic and wet oxidation of phenol catalyzed by non-promoted and potassium-promoted manganese/cerium oxide, *J. Hazard. Mater.* 138 (2006) 325–330.
- [56] F. Arena, J. Negro, A. Parmaliana, L. Spadaro, G. Trunfio, Improved MnCeO<sub>x</sub> systems for the catalytic wet oxidation (CWO) of phenol in wastewater streams, *Ind. Eng. Chem. Res.* 46 (2007) 6724–6731.
- [57] F. Arena, G. Trunfio, J. Negro, L. Spadaro, Synthesis of highly dispersed MnCeO<sub>x</sub> catalysts via a novel “redox-precipitation” route, *Mater. Res. Bull.* 43 (2008) 539–545.
- [58] F. Arena, G. Trunfio, J. Negro, L. Spadaro, Optimization of the MnCeO<sub>x</sub> system for the catalytic wet oxidation of phenol with oxygen (CWAO), *Appl. Catal. B: Environ.* 85 (2008) 40–47.
- [59] S.X. Yang, W.P. Zhu, J.B. Wang, Z.X. Chen, Catalytic wet air oxidation of phenol over CeO<sub>2</sub>-TiO<sub>2</sub> catalyst in the batch reactor and the packed-bed reactor, *J. Hazard. Mater.* 153 (2008) 1248–1253.
- [60] A. Quintanilla, J.A. Casas, J.A. Zazo, A.F. Mohedano, J.J. Rodriguez, Wet air oxidation of phenol at mild conditions with a Fe/activated carbon catalyst, *Appl. Catal. B: Environ.* 62 (2006) 115–120.
- [61] A. Quintanilla, J.A. Casas, A.F. Mohedano, J.J. Rodriguez, Reaction pathway of the catalytic wet air oxidation of phenol with a Fe/activated carbon catalyst, *Appl. Catal. B: Environ.* 67 (2006) 206–216.
- [62] A. Quintanilla, J.A. Casas, J.J. Rodriguez, Catalytic wet air oxidation of phenol with modified activated carbons and Fe/activated carbon catalysts, *Appl. Catal. B: Environ.* 76 (2007) 135–145.
- [63] A. Quintanilla, N. Menendez, J. Tornero, J.A. Casas, J.J. Rodriguez, Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: influence on activity, selectivity and stability, *Appl. Catal. B: Environ.* 81 (2008) 105–114.
- [64] A. Pigamo, M. Besson, B. Blanc, P. Gallezot, A. Blackburn, O. Kozynchenko, S. Tennison, E. Crezee, F. Kapteijn, Effect of oxygen functional groups on synthetic carbons on liquid phase oxidation of cyclohexanone, *Carbon* 40 (2002) 1267–1278.
- [65] M. Besson, P. Gallezot, A. Perrard, C. Pinel, Active carbons as catalysts for liquid phase reactions, *Catal. Today* 102 (2005) 160–165.
- [66] P. Korovchenko, C. Donze, P. Gallezot, M. Besson, Oxidation of primary alcohols with air on carbon-supported platinum catalysts for the synthesis of aldehydes or acids, *Catal. Today* 121 (2007) 13–21.
- [67] Y. Matsumura, T. Urase, K. Yamamoto, T. Nunoura, Carbon catalyzed supercritical water oxidation of phenol, *J. Supercrit. Fluids* 22 (2002) 149–156.
- [68] S.L. Cao, G.H. Chen, X.J. Hu, P.L. Yue, Catalytic wet air oxidation of wastewater containing ammonia and phenol over activated carbon supported Pt catalysts, *Catal. Today* 88 (2003) 37–47.
- [69] F. Stuber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias, A. Fabregat, Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater, *Top. Catal.* 33 (2005) 3–50.
- [70] A. Santos, P. Yustos, S. Gomis, G. Ruiz, F. Garcia-Ochoa, Reaction network and kinetic modeling of wet oxidation of phenol catalyzed by activated carbon, *Chem. Eng. Sci.* 61 (2006) 2457–2467.
- [71] A. Santos, P. Yustos, T. Cordero, S. Gomis, S. Rodriguez, F. Garcia-Ochoa, Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization, *Catal. Today* 102 (2005) 213–218.
- [72] T. Cordero, J. Rodriguez-Mirasol, J. Bedia, S. Gomis, P. Yustos, F. Garcia-Ochoa, A. Santos, Activated carbon as catalyst in wet oxidation of phenol: effect of the oxidation reaction on the catalyst properties and stability, *Appl. Catal. B: Environ.* 81 (2008) 122–131.
- [73] S.X. Yang, X. Li, W.P. Zhu, J.B. Wang, C. Descorme, Catalytic activity, stability and structure of multi-walled carbon nanotubes in the wet air oxidation of phenol, *Carbon* 46 (2008) 445–452.
- [74] J.Y. Qin, Q.L. Zhang, K.T. Chuang, Catalytic wet oxidation of *p*-chlorophenol over supported noble metal catalysts, *Appl. Catal. B: Environ.* 29 (2001) 115–123.
- [75] N. Li, C. Descorme, M. Besson, Catalytic wet air oxidation of aqueous solution of 2-chlorophenol over Ru/zirconia catalysts, *Appl. Catal. B: Environ.* 71 (2007) 262–270.
- [76] N. Li, C. Descorme, M. Besson, Catalytic wet air oxidation of 2-chlorophenol over Ru loaded Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> solid solutions, *Appl. Catal. B: Environ.* 76 (2007) 92–100.
- [77] T. Yamada, S. Katoh, K. Sawada, Y. Kojima, S. Ozawa, H. Matsuda, T. Fukuta, Effects of alkaline reagent and Ru/TiO<sub>2</sub> catalyst on the decomposition of *o*-chlorophenol by wet oxidation, *Kag. Kog. Ronbunshu* 28 (2002) 559–564.
- [78] Y. Kojima, T. Fukuta, T. Yamada, M.S. Onyango, E.C. Bernardo, H. Matsuda, K. Yagishita, Catalytic wet oxidation of *o*-chlorophenol at mild temperatures under alkaline conditions, *Water Res.* 39 (2005) 29–36.
- [79] D. Posada, P. Betancourt, F. Liendo, J.L. Brito, Catalytic wet air oxidation of aqueous solutions of substituted phenols, *Catal. Lett.* 106 (2006) 81–88.
- [80] M.E. Suarez-Ojeda, F. Stuber, A. Fortuny, A. Fabregat, J. Carrera, J. Font, Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst, *Appl. Catal. B: Environ.* 58 (2005) 105–114.
- [81] M.E. Suarez-Ojeda, A. Fabregat, F. Stuber, A. Fortuny, J. Carrera, J. Font, Catalytic wet air oxidation of substituted phenols: temperature and pressure effect on the pollutant removal, the catalyst preservation and the biodegradability enhancement, *Chem. Eng. J.* 132 (2007) 105–115.
- [82] A. Santos, P. Yustos, S. Rodriguez, F. Garcia-Ochoa, Wet oxidation of phenol, cresols and nitrophenols catalyzed by activated carbon in acid and basic media, *Appl. Catal. B: Environ.* 65 (2006) 269–281.
- [83] J. Beltran-Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, Comparison of the degradation of *p*-hydroxybenzoic acid in aqueous solution by several oxidation processes, *Chemosphere* 42 (2001) 351–359.
- [84] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stuber, Catalytic wet air oxidation of phenol over active carbon catalyst—global kinetic modelling using simulated annealing, *Appl. Catal. B: Environ.* 67 (2006) 12–23.
- [85] S. Suwanprasop, A. Eftaxias, F. Stuber, I. Polaert, C. Julcour-Lebigue, H. Delmas, Scale-up and modeling of fixed-bed reactors for catalytic phenol oxidation over adsorptive active carbon, *Ind. Eng. Chem. Res.* 44 (2005) 9513–9523.
- [86] M.D. Gonzalez, E. Moreno, J. Quevedosarmiento, A. Ramoscormenzana, Studies on antibacterial activity of waste waters from olive oil mills (alpechin): inhibitory activity of phenolic and fatty acids, *Chemosphere* 20 (1990) 423–432.
- [87] D.P. Minh, G. Aubert, P. Gallezot, M. Besson, Degradation of olive oil mill effluents by catalytic wet air oxidation: 2-oxidation of *p*-hydroxyphenylacetic and *p*-hydroxybenzoic acids over Pt and Ru supported catalysts, *Appl. Catal. B: Environ.* 73 (2007) 236–246.
- [88] D.P. Minh, P. Gallezot, M. Besson, Treatment of olive oil mill wastewater by catalytic wet air oxidation 3. Stability of supported ruthenium catalysts during oxidation of model pollutant *p*-hydroxybenzoic acid in batch and continuous reactors, *Appl. Catal. B: Environ.* 75 (2007) 71–77.
- [89] M. Triki, D.P. Minh, Z. Ksibi, A. Ghorbel, M. Besson, Ruthenium catalysts supported on TiO<sub>2</sub> prepared by sol-gel way for *p*-hydroxybenzoic acid wet air oxidation, *J. Sol-Gel Sci. Technol.* 48 (2008) 344–349.
- [90] M. Triki, Z. Ksibi, A. Ghorbel, F. Medina, Preparation and characterization of CeO<sub>2</sub>-TiO<sub>2</sub> support for Ru catalysts: application in CWAO of *p*-hydroxybenzoic acid, *Microporous Mesoporous Mater.* 117 (2009) 431–435.
- [91] M. Yang, A.H. Xu, H.Z. Du, C.L. Sun, C. Li, Removal of salicylic acid on perovskite-type oxide LaFeO<sub>3</sub> catalyst in catalytic wet air oxidation process, *J. Hazard. Mater.* 139 (2007) 86–92.
- [92] J.B. Wang, W.P. Zhu, X.W. He, S.X. Yang, Catalytic wet air oxidation of acetic acid over different ruthenium catalysts, *Catal. Commun.* 9 (2008) 2163–2167.
- [93] F. Larachi, J. Pierre, A. Adnot, A. Bernis, Ce 3d XPS study of composite Ce<sub>x</sub>Mn<sub>1-x</sub>O<sub>2-y</sub> wet oxidation catalysts, *Appl. Surf. Sci.* 195 (2002) 236–250.



- [94] S. Hosokawa, H. Kanai, K. Utani, Y. Taniguchi, Y. Saito, S. Imamura, State of Ru on CeO<sub>2</sub> and its catalytic activity in the wet oxidation of acetic acid, *Appl. Catal. B: Environ.* 45 (2003) 181–187.
- [95] S.X. Yang, W.P. Zhu, Z.P. Jiang, Z.X. Chen, J.B. Wang, The surface properties and the activities in catalytic wet air oxidation over CeO<sub>2</sub>-TiO<sub>2</sub> catalysts, *Appl. Surf. Sci.* 252 (2006) 8499–8505.
- [96] J. Gaalová, J. Barbier, S. Rossignol, Ruthenium versus platinum on cerium materials in wet air oxidation of acetic acid, *J. Hazard. Mater.* 181 (2010) 633–639.
- [97] J. Mikulová, S. Rossignol, J. Barbier, D. Mesnard, C. Kappenstein, D. Duprez, Ruthenium and platinum catalysts supported on Ce, Zr, Pr-O mixed oxides prepared by soft chemistry for acetic acid wet air oxidation, *Appl. Catal. B: Environ.* 72 (2007) 1–10.
- [98] J. Mikulová, S. Rossignol, J. Barbier, D. Duprez, C. Kappenstein, Characterizations of platinum catalysts supported on Ce, Zr, Pr-oxides and formation of carbonate species in catalytic wet air oxidation of acetic acid, *Catal. Today* 124 (2007) 185–190.
- [99] J. Mikulová, J. Barbier, S. Rossignol, D. Mesnard, D. Duprez, C. Kappenstein, Wet air oxidation of acetic acid over platinum catalysts supported on cerium-based materials: influence of metal and oxide crystallite size, *J. Catal.* 251 (2007) 172–181.
- [100] H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Carbon supported platinum catalysts for catalytic wet air oxidation of refractory carboxylic acids, *Top. Catal.* 33 (2005) 59–68.
- [101] D.K. Lee, D.S. Kim, Catalytic wet air oxidation of carboxylic acids at atmospheric pressure, *Catal. Today* 63 (2000) 249–255.
- [102] E. Sève, G. Antonini, Treatment of municipal sewage fats by wet oxidation, *Chem. Eng. J.* 76 (2000) 179–187.
- [103] B. Renard, J. Barbier, D. Duprez, S. Durecu, Catalytic wet air oxidation of stearic acid on cerium oxide supported noble metal catalysts, *Appl. Catal. B: Environ.* 55 (2005) 1–10.
- [104] S. Royer, B. Levasseur, H. Alamdari, J. Barbier, D. Duprez, S. Kaliaguine, Mechanism of stearic acid oxidation over nanocrystalline La<sub>1-x</sub>A<sub>x</sub>BO<sub>3</sub> (A<sup>+</sup>=Sr, Ce; B=Co, Mn): the role of oxygen mobility, *Appl. Catal. B: Environ.* 80 (2008) 51–61.
- [105] P.K. Barton, J.W. Atwater, Nitrous oxide emissions and the anthropogenic nitrogen in wastewater and solid waste, *J. Environ. Eng.-ASCE* 128 (2002) 137–150.
- [106] S.D. Hafner, J.J. Bisogni, W.J. Jewell, Measurement of un-ionized ammonia in complex mixtures, *Environ. Sci. Technol.* 40 (2006) 1597–1602.
- [107] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, *Appl. Catal. B: Environ.* 16 (1998) 31–42.
- [108] R. Sauleda, E. Brillas, Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe<sup>2+</sup> and UVA light, *Appl. Catal. B: Environ.* 29 (2001) 135–145.
- [109] S.H. Lin, S.J. Ho, C.L. Wu, Kinetic and performance characteristics of wet air oxidation of high-concentration wastewater, *Ind. Eng. Chem. Res.* 35 (1996) 307–314.
- [110] G. Ersöz, S. Atalay, Low-pressure catalytic wet air oxidation of aniline over Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub>, *Ind. Eng. Chem. Res.* 49 (2010) 1625–1630.
- [111] J. Barbier, L. Oliviero, B. Renard, D. Duprez, Catalytic wet air oxidation of ammonia over M/CeO<sub>2</sub> catalysts in the treatment of nitrogen-containing pollutants, *Catal. Today* 75 (2002) 29–34.
- [112] G.R. Reddy, V.V. Mahajani, Insight into wet oxidation of aqueous aniline over a Ru/SiO<sub>2</sub> catalyst, *Ind. Eng. Chem. Res.* 44 (2005) 7320–7328.
- [113] J. Garcia, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Carbon nanotube supported ruthenium catalysts for the treatment of high strength wastewater with aniline using wet air oxidation, *Carbon* 44 (2006) 2384–2391.
- [114] J. Garcia, H.T. Gomes, P. Serp, P. Kalck, J.L. Figueiredo, J.L. Faria, Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds, *Catal. Today* 102 (2005) 101–109.
- [115] H.T. Gomes, B.F. Machado, A. Ribeiro, I. Moreira, M. Rosario, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, Catalytic properties of carbon materials for wet oxidation of aniline, *J. Hazard. Mater.* 159 (2008) 420–426.
- [116] H.T. Gomes, P. Selvam, S.E. Dapurkar, J.L. Figueiredo, J.L. Faria, Transition metal (Cu, Cr, and V) modified MCM-41 for the catalytic wet air oxidation of aniline, *Microporous Mesoporous Mater.* 86 (2005) 287–294.
- [117] R. Levi, M. Milman, M.V. Landau, A. Brenner, M. Herskowitz, Catalytic wet air oxidation of aniline with nanocasted Mn-Ce-oxide catalyst, *Environ. Sci. Technol.* 42 (2008) 5165–5170.
- [118] R. Ganesh, G.D. Boardman, D. Michelsen, Fate of azo dyes in sludges, *Water Res.* 28 (1994) 1367–1376.
- [119] P. Ekcici, G. Leupold, H. Parlar, Degradability of selected azo dye metabolites in activated sludge systems, *Chemosphere* 44 (2001) 721–728.
- [120] A. Rodríguez, J. Garcia, G. Ovejero, M. Mestanza, Wet air and catalytic wet air oxidation of several azodyes from wastewaters: the beneficial role of catalysis, *Water Sci. Technol.* 60 (2009) 1989–1999.
- [121] A. Santos, P. Yustos, S. Rodríguez, F. Garcia-Ochoa, M. de Gracia, Decolorization of textile dyes by wet oxidation using activated carbon as catalyst, *Ind. Eng. Chem. Res.* 46 (2007) 2423–2427.
- [122] N. Mizuno, M. Misono, Heterogeneous catalysis, *Chem. Rev.* 98 (1998) 199–217.
- [123] S. Zhao, X.H. Wang, M.X. Huo, Catalytic wet air oxidation of phenol with air and micellar molybdoyanadophosphoric polyoxometalates under room condition, *Appl. Catal. B: Environ.* 97 (2010) 127–134.
- [124] I. Arslan-Alaton, J.L. Ferry, Application of polyoxotungstates as environmental catalysts: wet air oxidation of acid dye Orange II, *Dyes Pigment.* 54 (2002) 25–36.
- [125] Y. Zhang, D.L. Li, Y. Chen, X.H. Wang, S.T. Wang, Catalytic wet air oxidation of dye pollutants by polyoxomolybdate nanotubes under room condition, *Appl. Catal. B: Environ.* 86 (2009) 182–189.
- [126] J.G. Huang, X.H. Wang, S. Li, Y. Wang, ZnO/MoO<sub>3</sub> mixed oxide nanotube: a highly efficient and stable catalyst for degradation of dye by air under room conditions, *Appl. Surf. Sci.* 257 (2010) 116–121.
- [127] Y. Liu, D.Z. Sun, Development of Fe<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> as catalyst for catalytic wet air oxidation of methyl orange azo dye under room condition, *Appl. Catal. B: Environ.* 72 (2007) 205–211.
- [128] H. Ma, Q. Zhuo, B. Wang, Characteristics of CuO-MoO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> catalyst and its catalytic wet oxidation (CWO) of dye wastewater under extremely mild conditions, *Environ. Sci. Technol.* 41 (2007) 7491–7496.
- [129] G. Deiber, J.N. Foussard, H. Debellfontaine, Removal of nitrogenous compounds by catalytic wet air oxidation. Kinetic study, *Environ. Pollut.* 96 (1997) 311–319.
- [130] J.Y. Qin, K. Aika, Catalytic wet air oxidation of ammonia over alumina supported metals, *Appl. Catal. B: Environ.* 16 (1998) 261–268.
- [131] T.L. Huang, J.M. Macinnes, K.R. Cliffe, Nitrogen removal from wastewater by a catalytic oxidation method, *Water Res.* 35 (2001) 2113–2120.
- [132] R. Ukropec, B.F.M. Kuster, J.C. Schouten, R.A. van Santen, Low temperature oxidation of ammonia to nitrogen in liquid phase, *Appl. Catal. B: Environ.* 23 (1999) 45–57.
- [133] J. Taguchi, T. Okuhara, Selective oxidative decomposition of ammonia in neutral water to nitrogen over titania-supported platinum or palladium catalyst, *Appl. Catal. A: Gen.* 194 (2000) 89–97.
- [134] D.K. Lee, Mechanism and kinetics of the catalytic oxidation of aqueous ammonia to molecular nitrogen, *Environ. Sci. Technol.* 37 (2003) 5745–5749.
- [135] D.K. Lee, J.S. Cho, W.L. Yoon, Catalytic wet oxidation of ammonia: why is N<sub>2</sub> formed preferentially against NO<sub>3</sub><sup>-</sup>? *Chemosphere* 61 (2005) 573–578.
- [136] C.M. Hung, Catalytic wet oxidation of ammonia solution: activity of the nanoscale platinum-palladium-rhodium composite oxide catalyst, *J. Hazard. Mater.* 163 (2009) 180–186.
- [137] C.M. Hung, J.C. Lou, C.H. Lin, Catalytic wet oxidation of ammonia solution: activity of the copper-lanthanum-cerium composite catalyst, *J. Environ. Eng.-ASCE* 130 (2004) 193–200.
- [138] C.M. Hung, The effect of the calcination temperature on the activity of Cu-La-Ce composite metal catalysts for the catalytic wet oxidation of ammonia solution, *Powder Technol.* 191 (2009) 21–26.
- [139] C.M. Hung, Catalytic wet oxidation of ammonia solution: activity of the Cu-La-Ce/cordierite composite catalyst, *Environ. Eng. Sci.* 26 (2009) 351–358.
- [140] L. Kundakovic, M. Flytzani-Stephanopoulos, Reduction characteristics of copper oxide in cerium and zirconium oxide systems, *Appl. Catal. A: Gen.* 171 (1998) 13–29.
- [141] C.M. Hung, Effect of calcination temperature on activity of Cu-ACF catalysts in catalytic wet oxidation of ammonia solution, *Environ. Eng. Sci.* 25 (2008) 951–958.
- [142] C.M. Hung, Activity of Cu-activated carbon fiber catalyst in wet oxidation of ammonia solution, *J. Hazard. Mater.* 166 (2009) 1314–1320.
- [143] C.L. Mangun, K.R. Benak, M.A. Daley, J. Economy, Oxidation of activated carbon fibers: effect on pore size, surface chemistry, and adsorption properties, *Chem. Mat.* 11 (1999) 3476–3483.
- [144] S. Villar-Rodil, F. Suarez-Garcia, J.L. Paredes, A. Martinez-Alonso, J.M.D. Tascon, Activated carbon materials of uniform porosity from polyaramid fibers, *Chem. Mat.* 17 (2005) 5893–5908.
- [145] S.R. de Miguel, J.I. Vilella, E.L. Jablonski, O.A. Scelza, C.S.M. de Lecea, A. Linares-Solano, Preparation of Pt catalysts supported on activated carbon felts (ACF), *Appl. Catal. A: Gen.* 232 (2002) 237–246.
- [146] J. Przepiorski, A.W. Morawski, A. Oya, Method for preparation of copper-coated carbon material, *Chem. Mat.* 15 (2003) 862–865.
- [147] S. Kaewpuang-Ngam, K. Inazu, K.I. Aika, Selective wet air oxidation of diluted aqueous ammonia solutions over co-precipitated transition metal-aluminium catalysts, *Res. Chem. Intermed.* 28 (2002) 471–477.
- [148] S. Kaewpuang-Ngam, K. Inazu, T. Kobayashi, K.I. Aika, Selective wet-air oxidation of diluted aqueous ammonia solutions over supported Ni catalysts, *Water Res.* 38 (2004) 778–782.
- [149] A. Pintar, M. Besson, P. Gallezot, Catalytic wet air oxidation of Kraft bleaching plant effluents in the presence of titania and zirconia supported ruthenium, *Appl. Catal. B: Environ.* 30 (2001) 123–139.
- [150] A. Pintar, M. Besson, P. Gallezot, Catalytic wet air oxidation of Kraft bleach plant effluents in a trickle-bed reactor over a Ru/TiO<sub>2</sub> catalyst, *Appl. Catal. B: Environ.* 31 (2001) 275–290.
- [151] A. Pintar, G. Bercic, M. Besson, P. Gallezot, Catalytic wet-air oxidation of industrial effluents: total mineralization of organics and lumped kinetic modelling, *Appl. Catal. B: Environ.* 47 (2004) 143–152.
- [152] D.P. Minh, P. Gallezot, S. Azabou, S. Sayadi, M. Besson, Catalytic wet air oxidation of olive oil mill effluents: 4. Treatment and detoxification of real effluents, *Appl. Catal. B: Environ.* 84 (2008) 749–757.
- [153] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catalytic wet air oxidation of olive mill wastewater, *Catal. Today* 124 (2007) 254–259.
- [154] M. Yang, Y. Sun, A.H. Xu, X.Y. Lu, H.Z. Du, C.L. Sun, C. Li, Catalytic wet air oxidation of coke-plant wastewater on ruthenium-based eggshell catalysts in a bubbling bed reactor, *Bull. Environ. Contam. Toxicol.* 79 (2007) 66–70.

- [155] L.H. Han, J. Zhu, J. Kang, Y.H. Liang, Y. Sun, Catalytic wet air oxidation of high-strength organic coking wastewater, *Asia-Pac. J. Chem. Eng.* 4 (2009) 624–627.
- [156] A. Rodríguez, G. Ovejero, M.D. Romero, C. Diaz, M. Barreiro, J. Garcia, Catalytic wet air oxidation of textile industrial wastewater using metal supported on carbon nanofibers, *J. Supercrit. Fluids* 46 (2008) 163–172.
- [157] K. Belkacemi, F. Larachi, S. Hamoudi, A. Sayari, Catalytic wet oxidation of high-strength alcohol-distillery liquors, *Appl. Catal. A: Gen.* 199 (2000) 199–209.
- [158] D. Goi, C. de Leitenburg, G. Dolcetti, A. Trovarelli, COD and AOX abatement in catalytic wet oxidation of halogenated liquid wastes using CeO<sub>2</sub>-based catalysts, *J. Alloy. Compd.* 408 (2006) 1136–1140.
- [159] W.M. Liu, Y.Q. Hu, S.T. Tu, Active carbon-ceramic sphere as support of ruthenium catalysts for catalytic wet air oxidation (CWAO) of resin effluent, *J. Hazard. Mater.* 179 (2010) 545–551.
- [160] S.X. Yang, Z.Q. Liu, X.H. Huang, B.P. Zhang, Wet air oxidation of epoxy acrylate monomer industrial wastewater, *J. Hazard. Mater.* 178 (2010) 786–791.
- [161] G.B. Tabrizi, M. Mehrvar, Integration of advanced oxidation technologies and biological processes: recent developments, trends, and advances, *J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng.* 39 (2004) 3029–3081.
- [162] D. Mantzavinos, E. Psillakis, Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment, *J. Chem. Technol. Biotechnol.* 79 (2004) 431–454.
- [163] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, J.A. Casas, J.J. Rodriguez, Evolution of toxicity upon wet catalytic oxidation of phenol, *Environ. Sci. Technol.* 38 (2004) 133–138.
- [164] M.E. Suarez-Ojeda, A. Guisasaola, J.A. Baeza, A. Fabregat, F. Stuber, A. Fortuny, J. Font, J. Carrera, Integrated catalytic wet air oxidation and aerobic biological treatment in a municipal WWTP of a high-strength o-cresol wastewater, *Chemosphere* 66 (2007) 2096–2105.
- [165] M.E. Suarez-Ojeda, J. Kim, J. Carrera, I.S. Metcalfe, J. Font, Catalytic and non-catalytic wet air oxidation of sodium dodecylbenzene sulfonate: kinetics and biodegradability enhancement, *J. Hazard. Mater.* 144 (2007) 655–662.
- [166] A. Santos, P. Yustos, S. Rodriguez, F. Vicente, A. Romero, Detoxification kinetic modeling for nonbiodegradable wastewaters: an ecotoxicity lumping approach, *Ind. Eng. Chem. Res.* 47 (2008) 8639–8644.
- [167] J. Kang, W. Zhan, D. Li, X. Wang, J. Song, D. Liu, Integrated catalytic wet air oxidation and biological treatment of wastewater from Vitamin B6 production, *Phys. Chem. Earth* (2010), doi:10.1016/j.pce.2010.03.043.
- [168] F.J. Rivas, S.T. Kolaczowski, F.J. Beltran, D.B. McLurgh, Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts, *J. Chem. Technol. Biotechnol.* 74 (1999) 390–398.
- [169] F.J. Rivas, R. Garcia, J.F. Garcia-Araya, O. Gimeno, Promoted wet air oxidation of polynuclear aromatic hydrocarbons, *J. Hazard. Mater.* 153 (2008) 792–798.
- [170] A. Rubalcaba, M.E. Suárez-Ojeda, J. Carrera, J. Font, F. Stüber, C. Bengoa, A. Fortuny, A. Fabregat, Biodegradability enhancement of phenolic compounds by Hydrogen Peroxide Promoted Catalytic Wet Air Oxidation, *Catal. Today* 124 (2007) 191–197.
- [171] A. Quintanilla, J.A. Casas, J.J. Rodriguez, Hydrogen peroxide-promoted-CWAO of phenol with activated carbon, *Appl. Catal. B: Environ.* 93 (2010) 339–345.
- [172] H. Ohta, S. Goto, H. Teshima, Liquid-phase oxidation of phenol in a rotating catalytic basket reactor, *Ind. Eng. Chem. Fundam.* 19 (1980) 180–185.
- [173] D. Mantzavinos, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Catalytic wet oxidation of *p*-coumaric acid: partial oxidation intermediates, reaction pathways and catalyst leaching, *Appl. Catal. B: Environ.* 7 (1996) 379–396.
- [174] A. Eftaxias, J. Font, A. Fortuny, J. Giral, A. Fabregat, F. Stuber, Kinetic modelling of catalytic wet air oxidation of phenol by simulated annealing, *Appl. Catal. B: Environ.* 33 (2001) 175–190.
- [175] A. Santos, P. Yustos, A. Quintanilla, S. Rodriguez, F. Garcia-Ochoa, Route of the catalytic oxidation of phenol in aqueous phase, *Appl. Catal. B: Environ.* 39 (2002) 97–113.
- [176] D. Mantzavinos, E. Lauer, R. Hellenbrand, A.G. Livingston, I.S. Metcalfe, Wet oxidation as a pretreatment method for wastewaters contaminated by bioreistant organics, *Water Sci. Technol.* 36 (1997) 109–116.
- [177] F.J. Rivas, S.T. Kolaczowski, F.J. Beltran, D.B. McLurgh, Development of a model for the wet air oxidation of phenol based on a free radical mechanism, *Chem. Eng. Sci.* 53 (1998) 2575–2586.
- [178] D.A. Patterson, I.S. Metcalfe, F. Xiong, A.G. Livingston, Wet air oxidation of linear alkylbenzene sulfonate 2. Effect of pH, *Ind. Eng. Chem. Res.* 40 (2001) 5517–5525.
- [179] R. Robert, S. Barbati, N. Ricc, M. Ambrosio, Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterization of hydrogen peroxide, *Water Res.* 36 (2002) 4821–4829.
- [180] J. Tardio, S. Bhargava, S. Eyer, M. Sumich, D.B. Akolekar, Interactions between specific organic compounds during catalytic wet oxidation of Bayer liquor, *Ind. Eng. Chem. Res.* 43 (2004) 847–851.
- [181] I.I. Raffainer, P.R. von Rohr, Promoted wet oxidation of the azo dye orange II under mild conditions, *Ind. Eng. Chem. Res.* 40 (2001) 1083–1089.
- [182] M.J. Birchmeier, C.G. Hill, C.J. Houtman, R.H. Atalla, I.A. Weinstock, Enhanced wet air oxidation: synergistic rate acceleration upon effluent recirculation, *Ind. Eng. Chem. Res.* 39 (2000) 55–64.
- [183] D. Mantzavinos, A.G. Livingston, R. Hellenbrand, I.S. Metcalfe, Wet air oxidation of polyethylene glycols; mechanisms, intermediates and implications for integrated chemical-biological wastewater treatment, *Chem. Eng. Sci.* 51 (1996) 4219–4235.
- [184] P.D. Vaidya, V.V. Mahajani, Insight into sub-critical wet oxidation of phenol, *Adv. Environ. Res.* 6 (2002) 429–439.
- [185] B. Stoffer, G. Luft, Influence of the radical scavenger *t*-butanol on the wet air oxidation of *p*-toluenesulfonic acid, *Chem. Eng. Technol.* 22 (1999) 409–412.
- [186] C.M.J. Chang, S.S. Li, C.M. Ko, Catalytic wet oxidations of phenol-contaminated and *p*-chlorophenol-contaminated waters, *J. Chem. Technol. Biotechnol.* 64 (1995) 245–252.
- [187] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, London, 1981.
- [188] F. Cavani, F. Trifiro, Classification of industrial catalysts and catalysis for the petrochemical industry, *Catal. Today* 34 (1997) 269–279.
- [189] J. Novakova, Isotopic exchange of oxygen <sup>18</sup>O between the gaseous phase and oxide catalysts, *Catal. Rev.-Sci. Eng.* 4 (1971) 77–113.
- [190] A. Sadana, J.R. Katzer, Involvement of free-radicals in aqueous-phase catalytic-oxidation of phenol over copper oxide, *J. Catal.* 35 (1974) 140–152.
- [191] A. Pintar, J. Levec, Catalytic liquid-phase oxidation of phenol aqueous solutions. A kinetic investigation, *Ind. Eng. Chem. Res.* 33 (1994) 3070–3077.
- [192] A. Pintar, J. Levec, Catalytic oxidation of aqueous *p*-chlorophenol and *p*-nitrophenol solutions, *Chem. Eng. Sci.* 49 (1994) 4391–4407.
- [193] A. Sadana, Analysis of heterogeneously catalyzed free-radical oxidation of phenol in aqueous-solution, *Ind. Eng. Chem. Process Des. Dev.* 18 (1979) 50–56.
- [194] A. Sadana, J.R. Katzer, Catalytic oxidation of phenol in aqueous solution over copper oxide, *Ind. Eng. Chem. Fundam.* 13 (1974) 127–134.
- [195] H.R. Devlin, I.J. Harris, Mechanism of the oxidation of aqueous phenol with dissolved-oxygen, *Ind. Eng. Chem. Fundam.* 23 (1984) 387–392.
- [196] J. Levec, J.M. Smith, Oxidation of acetic-acid solutions in a trickle-bed reactor, *AIChE J.* 22 (1976) 159–168.
- [197] D. Duprez, F. Delanoë, J. Barbier, P. Isnard, G. Blanchard, Catalytic oxidation of organic compounds in aqueous media, *Catal. Today* 29 (1996) 317–322.
- [198] Z.P.G. Masende, B.F.M. Kuster, K.J. Ptasiński, F. Janssen, J.H.Y. Katima, J.C. Schouten, Platinum catalysed wet oxidation of phenol in a stirred slurry reactor—the role of oxygen and phenol loads on reaction pathways, *Catal. Today* 79 (2003) 357–370.
- [199] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, Lower toxicity route in catalytic wet oxidation of phenol at basic pH by using bicarbonate media, *Appl. Catal. B: Environ.* 53 (2004) 181–194.
- [200] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, Influence of pH on the wet oxidation of phenol with copper catalyst, *Top. Catal.* 33 (2005) 181–192.
- [201] A. Fortuny, C. Bengoa, J. Font, F. Castells, A. Fabregat, Water pollution abatement by catalytic wet air oxidation in a trickle bed reactor, *Catal. Today* 53 (1999) 107–114.
- [202] R.V. Shende, J. Levec, Wet oxidation kinetics of refractory low molecular mass carboxylic acids, *Ind. Eng. Chem. Res.* 38 (1999) 3830–3837.
- [203] A. Santos, P. Yustos, B. Durban, F. Garcia-Ochoa, Catalytic wet oxidation of phenol: kinetics of phenol uptake, *Environ. Sci. Technol.* 35 (2001) 2828–2835.
- [204] C.B. Maugans, A. Alkerman, Catalytic wet oxidation of phenol in a trickle bed reactor over a Pt/TiO<sub>2</sub> catalyst, *Water Res.* 37 (2003) 319–328.
- [205] Q. Wu, X.J. Hu, P.L. Yue, Kinetics study on heterogeneous catalytic wet air oxidation of phenol using copper/activated carbon catalyst, *Int. J. Chem. Reactor Eng.* 3 (2005) A29.
- [206] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, F. Stuber, Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst, *J. Chem. Technol. Biotechnol.* 80 (2005) 677–687.
- [207] J. Guo, M. Al-Dahhan, Kinetics of wet air oxidation of phenol over a novel catalyst, *Ind. Eng. Chem. Res.* 42 (2003) 5473–5481.
- [208] S. Hamoudi, F. Larachi, A. Sayari, Wet oxidation of phenolic solutions over heterogeneous catalysts: degradation profile and catalyst behavior, *J. Catal.* 177 (1998) 247–258.
- [209] J.C. Beziat, M. Besson, P. Gallezot, S. Durecu, Catalytic wet air oxidation on a Ru/TiO<sub>2</sub> catalyst in a trickle-bed reactor, *Ind. Eng. Chem. Res.* 38 (1999) 1310–1315.
- [210] F. Arena, C. Italian, A. Raneri, C. Saja, Mechanistic and kinetic insights into the wet air oxidation of phenol with oxygen (CWAO) by homogeneous and heterogeneous transition-metal catalysts, *Appl. Catal. B: Environ.* 99 (2010) 321–328.
- [211] T.L. Gunale, V.V. Mahajani, An insight into Ru/TiO<sub>2</sub> catalyzed wet air oxidation of *N*-ethylethanolamine in an aqueous solution, *Chem. Eng. J.* 159 (2010) 17–23.
- [212] L.X. Li, P.S. Chen, E.F. Gloyna, Generalized kinetic-model for wet oxidation of organic-compounds, *AIChE J.* 37 (1991) 1687–1697.
- [213] A. Cybulski, J. Trawczynski, Catalytic wet-air oxidation of a chemical plant wastewater over platinum-based catalysts, *Water Environ. Res.* 78 (2006) 12–18.
- [214] K. Belkacemi, F. Larachi, A. Sayari, Lumped kinetics for solid-catalyzed wet oxidation: a versatile model, *J. Catal.* 193 (2000) 224–237.
- [215] S. Hamoudi, K. Belkacemi, F. Larachi, Catalytic oxidation of aqueous phenolic solutions catalyst deactivation and kinetics, *Chem. Eng. Sci.* 54 (1999) 3569–3576.
- [216] A. Cybulski, J. Trawczynski, Catalytic wet air oxidation of phenol over platinum and ruthenium catalysts, *Appl. Catal. B: Environ.* 47 (2004) 1–13.
- [217] A. Pintar, J. Levec, Catalytic liquid-phase oxidation of refractory organics in waste water, *Chem. Eng. Sci.* 47 (1992) 2395–2400.
- [218] A. Pintar, J. Levec, Catalytic oxidation of organics in aqueous solutions. I. Kinetics of phenol oxidation, *J. Catal.* 135 (1992) 345–357.
- [219] S. Keav, A. Martin, J. Barbier, D. Duprez, Nature of the deposit formed during catalytic wet air oxidation of phenol, *C. R. Chim.* 13 (2010) 508–514.

- [220] D.K. Lee, D.S. Kim, T.H. Kim, Y.K. Lee, S.E. Jeong, N.T. Le, M.J. Cho, S.D. Henam, Deactivation of Pt catalysts during wet oxidation of phenol, *Catal. Today* 154 (2010) 244–249.
- [221] S. Keav, A. Martin, J. Barbier, D. Duprez, Deactivation and reactivation of noble metal catalysts tested in the Catalytic Wet Air Oxidation of phenol, *Catal. Today* 151 (2010) 143–147.
- [222] A. Alejandre, F. Medina, X. Rodriguez, P. Salagre, Y. Cesteros, J.E. Sueiras, Cu/Ni/Al layered double hydroxides as precursors of catalysts for the wet air oxidation of phenol aqueous solutions, *Appl. Catal. B: Environ.* 30 (2001) 195–207.
- [223] A. Alejandre, F. Medina, P. Salagre, A. Fabregat, J.E. Sueiras, Characterization and activity of copper and nickel catalysts for the oxidation of phenol aqueous solutions, *Appl. Catal. B: Environ.* 18 (1998) 307–315.
- [224] A. Alejandre, F. Medina, A. Fortuny, P. Salagre, J.E. Sueiras, Characterisation of copper catalysts and activity for the oxidation of phenol aqueous solutions, *Appl. Catal. B: Environ.* 16 (1998) 53–67.
- [225] C. Miro, A. Alejandre, A. Fortuny, C. Bengoa, J. Font, A. Fabregat, Aqueous phase catalytic oxidation of phenol in a trickle bed reactor: effect of the pH, *Water Res.* 33 (1999) 1005–1013.
- [226] R. Kouraichi, J.J. Delgado, J.D. Lopez-Castro, M. Stitou, J.M. Rodriguez-Izquierdo, M.A. Cauqui, Deactivation of Pt/MnO<sub>x</sub>-CeO<sub>2</sub> catalysts for the catalytic wet oxidation of phenol: formation of carbonaceous deposits and leaching of manganese, *Catal. Today* 154 (2010) 195–201.
- [227] K.H. Kim, S.K. Ihm, Characteristics of titania supported copper oxide catalysts for wet air oxidation of phenol, *J. Hazard. Mater.* 146 (2007) 610–616.
- [228] A. Santos, P. Yustos, B. Durban, F. Garcia-Ochoa, Oxidation of phenol in aqueous solution with copper catalysts, *Catal. Today* 66 (2001) 511–517.
- [229] A. Santos, P. Yustos, A. Quintanilla, G. Ruiz, F. Garcia-Ochoa, Study of the copper leaching in the wet oxidation of phenol with CuO-based catalysts: causes and effects, *Appl. Catal. B: Environ.* 61 (2005) 323–333.
- [230] S. Hamoudi, A. Sayari, K. Belkacemi, L. Bonneviot, F. Larachi, Catalytic wet oxidation of phenol over Pt<sub>x</sub>Ag<sub>1-x</sub>MnO<sub>2</sub>/CeO<sub>2</sub> catalysts, *Catal. Today* 62 (2000) 379–388.
- [231] S.T. Hussain, A. Sayari, F. Larachi, Novel K-doped Mn-Ce-O wet oxidation catalysts with enhanced stability, *J. Catal.* 201 (2001) 153–157.
- [232] S.T. Hussain, A. Sayari, F. Larachi, Enhancing the stability of Mn-Ce-O WETOX catalysts using potassium, *Appl. Catal. B: Environ.* 34 (2001) 1–9.
- [233] S.T. Hussain, S. Jamil, M. Mazhar, Catalytic wet oxidation of phenol: the role of promoter and ceramic support, *Environ. Technol.* 30 (2009) 511–524.
- [234] R.J. Fenoglio, P.A. Massa, F.D. Ivorra, P.M. Haure, Conventional and wet proofed CuO/Al<sub>2</sub>O<sub>3</sub> catalysts for phenol oxidation: deactivation studies in a trickle bed reactor, *J. Chem. Technol. Biotechnol.* 82 (2007) 481–487.
- [235] P. Massa, F. Ivorra, P. Haure, R. Fenoglio, Optimized wet-proofed CuO/Al<sub>2</sub>O<sub>3</sub> catalysts for the oxidation of phenol solutions: enhancing catalytic stability, *Catal. Commun.* 10 (2009) 1706–1710.
- [236] G.R. Lumpkin, Crystal chemistry and durability of the spinel structure type in natural systems, *Prog. Nucl. Energy* 38 (2001) 447–454.
- [237] A. Alejandre, F. Medina, X. Rodriguez, P. Salagre, J.E. Sueiras, Preparation and activity of Cu–Al mixed oxides via hydrotalcite-like precursors for the oxidation of phenol aqueous solutions, *J. Catal.* 188 (1999) 311–324.
- [238] A.H. Xu, M. Yang, H.Z. Du, C.L. Sun, Influence of partial replacement of Cu by Fe on the CWO of phenol in the Cu<sub>0.5-x</sub>Fe<sub>x</sub>Zn<sub>0.5</sub>Al<sub>2</sub>O<sub>4</sub> spinel catalysts, *Catal. Commun.* 7 (2006) 513–517.
- [239] A.H. Xu, M. Yang, R.P. Qiao, H.Z. Du, C.L. Sun, Activity and leaching features of zinc-aluminum ferrites in catalytic wet oxidation of phenol, *J. Hazard. Mater.* 147 (2007) 449–456.
- [240] A.H. Xu, X.Y. Lu, M. Yang, H.Z. Du, C.L. Sun, Activity and stability of ZnFe<sub>0.25</sub>Al<sub>1.75</sub>O<sub>4</sub> catalyst in catalytic wet air oxidation of phenol, *Chin. J. Catal.* 28 (2007) 395–397.