# Catalytic Wet Air Oxidation (CWAO) of Industrial Wastewaters: Mechanistic Evidences, Catalyst Development and Kinetic Modeling

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**Abstract.** Huge water consumptions and pollutants releases in the environment urge effective water decontamination technologies, fostering extensive recycle and reuse of industrial process-water and wastewater. The heterogeneous catalytic wet air oxidation (CWAO) offers a practical solution to the problem of decontamination of industrial effluents characterised by high concentration of toxic-refractory compounds, which are also detrimental for the active sludge of biological systems. Therefore, this work shows the superior CWAO performance of a new class of *nanostructured* $MnCeO_x$ catalysts toward the mineralization of some common toxic and refractory industrial pollutants. Mechanistic and kinetic evidences are summarised into a Langmuir-Hinshelwood reaction mechanism, leading to a formal kinetic model predicting the CWAO performance of nanostructured $MnCeO_x$ catalysts and optimum reaction conditions.

**Keywords:** Catalytic wet air oxidation (CWAO) · Nanocomposite MnCeOx catalysts · Toxic-Refractory wastewaters

## 1 Introduction

Since more than two decades, wastewater detoxification has become a topic of major concern, pressed by a constantly increasing world population and the consequent growth of water needs for agricultural and industrial purposes, both accounting for more than 90% of current global freshwater consumption [1]. This implies continuous depletion and pollution of natural resources, while ca. 700 million people globally lack access to safe water supply and ca. 2.4 billion are without access to basic sanitation [1]. Hence, new water-management policies are required in order to accomplish drastic cuts of water consumption by systematic application of suitable decontamination-remediation technologies, nowadays accounting for a global business worthy of ca. $625 billion and with an estimated growth annual rate of 4% [2]. In this context, the heterogeneous catalytic wet air oxidation (CWAO) offers a versatile and economically viable solution to the large-scale depollution of concentrated industrial wastewaters (COD > 10 g/L), especially those containing refractory and/or toxic compounds for the conventional biological treatment [3]. Although the CWAO technology could foster systematic recycle and reuse of process-waters and wastewaters, yet, its exploitation is still hindered by the

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lack of efficient, robust, and cost-effective catalysts alternative to supported noble-metals [4]. Therefore, this work is aimed at providing an outline of our most relevant research findings on the CWAO efficiency of *nanocomposite* $MnCeO_x$ catalysts in the range of 100–160 °C toward "probe" molecules (e.g., phenol and carboxylic acids), representative of some common classes of organic pollutants. Systematic kinetic studies highlight the mechanistic issues of the CWAO process, leading to a formal kinetic model accounting for catalyst performance and optimum reaction conditions.

## 2 Materials and Methods

Nanostructured $MnCeO_x$ catalysts (MxCy) with Ce/Mn (y/x) atomic ratios between 3/1 and 0 ($MnO_x$) were synthesised via the *redox-precipitation* route [5, 6]. A reference $MnCeO_x$ sample (Mn/Ce, 1) was prepared via co-precipitation of $MnCl_2$ and $CeCl_3$ (M1C1-P4) precursors [7], while a 5 wt% $Pt/CeO_2$ ($Pt_{at}/Ce_{at}$, 0.05) catalysts was obtained by incipient wetness impregnation of a high surface area ceria sample with a $Pt(NH_3)_4(NO_3)_2$ solution, and subsequent drying at 90 °C [8]. The list of the studied catalysts is given in Table 1.

**Table 1.** Physico-chemical properties of the studied catalysts

| Catalyst | Bulk composition | | | | | | SA ($m^2/g$) | PV ($cm^3/g$) | APD (nm) |
|---|---|---|---|---|---|---|---|---|---|
| | (wt%)[a] | | | (at.%) | | $Ce_{at}/Mn_{at}$ | | | |
| | $MnO_x$ | $CeO_x$ | $KO_x$ | Mn | Ce | | | | |
| M1C3 | 14.1 | 85.8 | 0.1 | 24.2 | 75.5 | 3.00 | 204 | 0.55 | 24 |
| M1C1 | 34.4 | 65.4 | 0.2 | 50.7 | 48.8 | 1.00 | 190 | 0.46 | 25 |
| M3C1 | 59.9 | 36.8 | 3.2 | 70.8 | 22.0 | 0.33 | 184 | 0.57 | 27 |
| M5C1 | 66.9 | 28.4 | 4.7 | 74.3 | 16.0 | 0.20 | 159 | 0.56 | 30 |
| M9C1 | 77.0 | 17.6 | 5.4 | 80.3 | 9.3 | 0.10 | 136 | 0.49 | 31 |
| M | 93.5 | – | 6.5 | 88.6 | 0.0 | 0.00 | 94 | 0.34 | 31 |

[a] Calculated as $MnO_2$, $CeO_2$ and $K_2O$.

CWAO tests in the range of 100–160 °C and total pressure of 1.0–1.8 MPa ($P_{O2}$, 0.9 MPa) were carried out in a PTFE-lined autoclave (0.25 L), equipped with a magnetic impeller (≈800 rpm). The reactor was loaded with an aqueous suspension (0.14 L) of the catalyst (5 g/L) and fed with a continuous $O_2$ flow at the rate of 0.1 *stp*·L $min^{-1}$. After heating at the reaction temperature, a concentrated substrate solution (0.01 L) was injected by a pressurized loop to give an initial concentration of 1 g/L ($R = w_{cat}/w_{sub}$, 5), unless otherwise specified.

## 3 Results and Discussions

The activity data in the CWAO of phenol (373 K) of $MnCeO_x$ catalysts (Mn/Ce, 1), prepared via *redox-precipitation* (M1C1-R4) and co-precipitation (M1C1-P4) methods, are compared in Fig. 1 in terms of phenol and TOC concentration *vs.* reaction time during two consecutive runs.

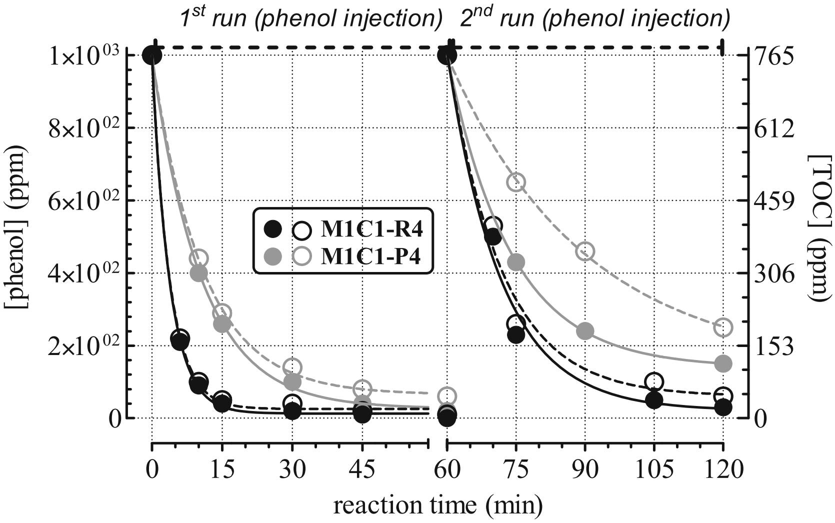

**Fig. 1.** CWAO activity data (T, 373 K; P, 1.0 MPa; R, 5) of the M1C1-R4 (black symbols) and M1C1-P4 catalysts (grey symbols); Phenol (full symbols) and TOC (open symbols) concentration *vs.* reaction time

The M1C1-R4 catalyst features a very high water purification efficiency probed by the complete (>95%) abatement of phenol and TOC in both first and second runs after 15 and 45 min, respectively. The M1C1-P4 system is considerably less active, since in the first run it attains a complete elimination of phenol and TOC after 1 h, and a partial removal of phenol (85%) and TOC (75%) in the 2nd run. Moreover, an almost instantaneous pH decrease to a value of 4.2 is recorded with the M1C1-R4 catalyst, while for the latter one a pH value of 4.9 is recorded after 30 min. This evidence is diagnostic of an incipient (partial) oxidation of the substrate and the consequent release of carboxylic acids (e.g., formic, oxalic, acetic) [4], being faster on the redox-precipitated system [5–7]. In spite of acidic pH, metal leaching is in both cases negligible, corresponding to less than 0.1% of manganese load.

The CWAO pattern of the M1C1-P4 catalyst is further compared with a typical $Pt/CeO_2$ system in Fig. 2 (T, 423 K; P, 1.4 MPa; R, 2), showing phenol and TOC conversion, $CO_2$ selectivity and pH during 6 h of reaction time. The $Pt/CeO_2$ system shows asymptotic growth of phenol and TOC conversion to final values of 55 and 45% respectively, along with $CO_2$ selectivity and pH values of 20 and 4%, respectively

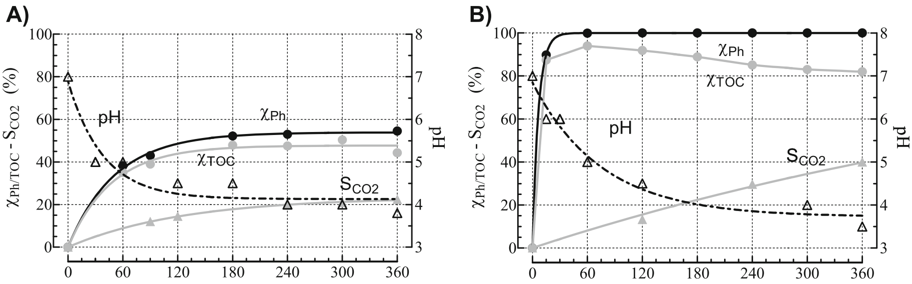

**Fig. 2.** CWAO activity data (T, 423 K; P, 1.4 MPa; R, 2) of Pt/$CeO_2$ (A) and M1C1-P4 catalysts (B)

(Fig. 2A). The M1C1-P4 catalyst has a considerably better performance, probed by the complete removal of phenol and a TOC abatement of 90% after 1 h; thereafter, the TOC conversion lowers slightly until a final value of 80%, when pH and $CO_2$ selectivity values of 3.5 and 40%, are recorded (Fig. 2B). Notably, in both cases experimental data signal significant gaps in C-mass balance (i.e., $S_{CO2}$-$X_{TOC}$), corresponding to 25 and 40% for Pt/$CeO_2$ and M1C1-P4 catalysts, respectively [4–8].

Thus, despite a different CWAO performance, the similar reactivity pattern of the studied catalysts is consistent with a *dual-site* Langmuir–Hinshelwood (L–H) reaction pathway, including a *fast* adsorption step, responsible for phenol and TOC conversion, following its *slow* surface oxidation (*r.d.s.*) on different surface sites (i.e., "α", "σ-O") [4, 7].

Indeed, the reaction scheme in Fig. 3 shows that both by-product release (e.g., C1-C2 acids) and catalyst fouling depend on side-reactions of the mineralization step (i.e., $CO_2$ formation), accounting for residual TOC and incipient catalyst deactivation [4, 7].

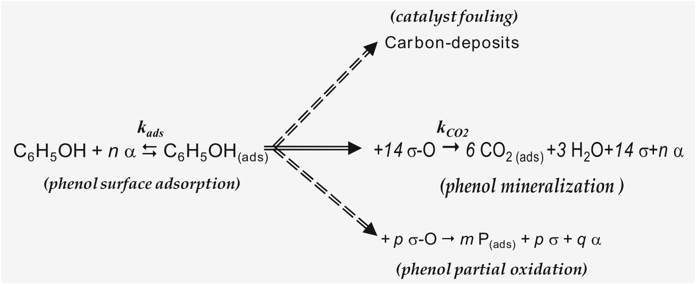

**Fig. 3.** Simplified reaction scheme of the heterogeneous CWAO of phenol

Furthermore, a thorough kinetic study of the CWAO of phenol has been devoted at ascertaining the influence of chemical composition on the reactivity pattern of the composite materials in view of catalyst optimization. Mechanistic evidences coming from the effects of catalyst load, oxygen pressure, temperature and substrate concentration have been summarised in a formal L-H kinetic model predicting the reactivity of nanostructured $MnCeO_x$ catalysts in the CWAO of phenol in the range of 100–160 °C.

## 4 Conclusions

- The heterogeneous Catalytic Wet Air Oxidation (CWAO) represents the most promising technology for purification of industrial wastewater.
- Catalyst development is the main drawback to the large scale application of the CWAO technology.
- Systematic studies on reaction mechanism and kinetics lead to development of a new class of nanostructured $MnCeO_x$ catalyst very efficient in the CWAO of toxic and refractory pollutants.
- Low-cost catalyst formulations coupled to high water-purification efficiency are key-factors for the large scale application of the CWAO technology.

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