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# Wet Air Oxidation of phenol over Pt and Ru catalysts supported on cerium-based oxides: Resistance to fouling and kinetic modelling

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## ABSTRACT

Ceria and doped ceria supported Pt and Ru catalysts were tested at 160 °C in the Catalytic Wet Air Oxidation (CWAO) of phenol. Catalysts were compared in terms of activity, selectivity and resistance towards fouling. The respective influences of metal phase and support were studied. Under the selected operating conditions, 100% phenol conversion could be reached. Contrary to what was expected, improved Oxygen Storage Capacities (OSC) accelerated the accumulation of adsorbed species on the catalyst surface, therefore limiting the catalytic performance. By contrast, high metal dispersions enhanced both the elimination of aqueous organic compounds and the degradation of heavy molecules involved in the catalyst fouling. The progressive decrease in activity induced by carbonaceous deposits could be kinetically modelled using a simple reaction scheme.

## 1. Introduction

Known since the early 20th century, the Wet Air Oxidation (WAO) process is particularly promising for the treatment of wastewaters containing highly concentrated, toxic or hardly biodegradable compounds [1]. WAO consists in oxidizing organic pollutants into nontoxic products (ultimately $CO_2$ and $H_2O$). In the absence of a catalyst, temperatures up to 320 °C and pressures up to 200 bar are necessary to attain acceptable conversions. The use of a catalyst significantly improves the efficiency of the process: Catalytic Wet Air Oxidation (CWAO) can be operated at temperatures and pressures below 200 °C and 30 bar, respectively.

Many heterogeneous catalytic systems have been considered for the reaction. Amongst them, supported Pt, Ru and Pd noble metals demonstrate high stability and activity. Due to their efficiency in processes involving redox reactions as well as their stability under acidic and oxidative conditions, cerium-based oxides are excellent candidates as supports for WAO catalysts. It was shown that ceria alone is able to convert more than 90% of aqueous phenol [2] and that its addition to certain formulations can greatly improve the catalytic performance [3]. Additionally, some cerium-based oxides, such as $MnO_2$–$CeO_2$, are extremely active in the oxidation of refractory compounds [4]. The efficiency of such catalytic systems comes from the oxygen transfer and storage properties of ceria, which result from the ability of Ce element to easily switch between +III and +IV oxidation states. The mobility of oxygen atoms can be improved by heat treatment, doping or the presence of noble metal species dispersed on the oxide surface [2,5].

Phenol is an intermediate in the oxidation of many aromatic compounds. Moreover, it is a toxic molecule resistant to biotreatment. Several authors determined the reaction pathway of the catalytic oxidation of aqueous phenol [6–8]. One of the most elaborated models, proposed by Rivas et al. [9], was based on elementary radical reactions (phenol oxidation is recognized to proceed via a free-radical mechanism [10]). The authors calculated unknown rate constants and verified that predicted concentration profiles were in agreement with experimental data. Eftaxias et al. [11] carried out a noteworthy kinetic study of phenol oxidation: a scheme comprising 7 reactions was considered and 31 parameters were simultaneously optimized. However, these reaction pathways do not take into account the formation of deactivating polymeric species. A few counterexamples can be found. Alejandre et al. [12] considered the direct polymerization of phenol. Masende et al. [13] proposed a particularly interesting scheme in which they specified desired and

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undesired reaction routes. Pintar and Levec [10] included the formation of heavy species from polymerization reactions involving glyoxal. More recently, Delgado et al. [14] included the formation and oxidation of the carbonaceous deposits as a parallel pathway for phenol degradation. Hamoudi et al. [15] as well as Arena et al. [16,17] proposed lumped reaction schemes taking account of adsorption and desorption steps of reactants and products as well as activity decline due to the formation and accumulation of carbonaceous materials over the catalytic surface.

This paper deals with CWAO of phenol in the presence of Pt and Ru catalysts supported on Ce-, Zr- and Pr-based oxides. It focuses on the respective influences of metal and support phases on activity and selectivity. Deactivation by fouling is considered and modelled via a simple reaction scheme.

## 2. Experimental

### 2.1. Catalyst preparation

$CeO_2$ (Ce), $Zr_{0.1}Ce_{0.9}O_2$ (ZrCe) and $Zr_{0.1}(Ce_{0.75}Pr_{0.25})_{0.9}O_2$ (ZrCePr) were used as supports in this study. Ce was a commercial HSA5 ceria provided by Rhodia and calcined in air at 650 or 800 °C. ZrCe and ZrCePr mixed oxides were synthesized following the sol–gel procedure described by Rossignol et al. [18]: an aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ and/or $Pr(NO_3)_3{\cdot}6H_2O$ was progressively added, at room temperature, to a solution of $Zr(OC_3H_7)_4$ in isopropanol. The resulting pseudo-gel was dried in a sand bath at 60 °C for 60 min and subsequently in a ventilated oven at 120 °C for 720 min. The powder was finally calcined in air at 400, 500, 650 or 800 °C for 300 min.

The metal phase was deposited by contacting the bare support with a precursor solution under pH conditions favouring the dispersion of metal species. Catalysts were prepared from $RuCl_3{\cdot}nH_2O$ in acidic medium or $Pt(NH_3)_4(OH)_2$ in alkaline medium. Metal contents were set at 1.25 wt% for Ru and 2.50 wt% for Pt. These values correspond to similar molar amounts of metal species. The mixture of precursor solution and support was stirred at 45 rpm for 240 min and evaporated under vacuum at 30 °C. Final catalysts were obtained after overnight drying at 120 °C followed by reduction in $H_2$ (30 mL $min^{-1}$) at 350 or 500 °C for 180 min.

Catalysts with different compositions and calcination/reduction temperatures were synthesized in order to evaluate the influence of the support, the metal phase and the particle size on activity and selectivity. The following notation system was used to name activated catalysts: MeSupp$T_{Calc}$-$T_{Red}$ where (i) Me is the deposited metal (Ru or Pt), (ii) Supp is the support (Ce, ZrCe or ZrCePr), (iii) $T_{Calc}$ (°C) is the calcination temperature of the support and (iv) $T_{Red}$ (°C) is the reduction temperature of the final catalyst.

### 2.2. Experimental set-up and procedure

Fouling is the major cause of deactivation of noble metal catalysts used in the CWAO of phenol [19,20]. Since this study focuses on deactivation, operating conditions accelerating the formation of fouling materials (low temperature, high phenol concentration) were selected. CWAO tests were performed in a 0.44 L batch reactor made of Hastelloy C22 alloy loaded with $V_{Liq}$ = 0.16 L of an aqueous solution containing phenol and the catalyst at respective concentrations of $C_{PhOH}$ = 2.098 g $L^{-1}$ and $C_{Cat}$ = 4 g $L^{-1}$. After a purge with helium, the reactor was heated up to the reaction temperature, typically $T$ = 160 °C. The stirring speed was set at $\omega$ = 1000 rpm. At the initial time of the reaction, 20 bars of pure $O_2$ were introduced into the reactor. The pressure was maintained constant throughout the experiment by regularly refilling with $O_2$. Gas phase and liquid phase samples were simultaneously and periodically collected for analysis. After 180 min of reaction, the reactor was cooled down to room temperature. The catalyst was recovered, washed with ultra-pure water and dried overnight at 120 °C.

As the reactor was not equipped with a cooling system and since phenol oxidation is an exothermic reaction, a slight increase in temperature (always smaller than 8 °C) was generally recorded, just after introduction of oxygen in the system. Temperature was always back to 160 °C within 2 min. This brief shift from the intended reaction temperature is not expected to significantly affect kinetic data. It is to be noted that, although maintaining constant the operating pressure by refilling oxygen, $CO_2$ is accumulating in the gas phase during the reaction ($CO_2$ partial pressure was about 1.5 bar at the end of the experiment with our best performing catalyst). The reproducibility of the experimental protocol was verified for several reference catalysts and the experimental error was found to be lower than 5%. The stirring speed and the mass of catalyst were varied according to well-known procedures [21] in order to confirm the absence of external mass transfer limitations under the selected conditions.

### 2.3. Analytical techniques

The amount of $CO_2$ in the gas phase was determined by gas chromatography (Varian 3900 GC equipped with a thermal conductivity detector and a Porapaq Q column). Calculations were made based on the peak surface areas of $CO_2$ and $O_2$ in the gas chromatogram as well as the temperature and the total pressure in the CWAO reactor. $CO_2$ in the liquid phase was quantified from the amount of gaseous $CO_2$ according to a previous study concerning aqueous/gaseous $CO_2$ equilibrium at different temperatures and at acidic pH [22]. Phenol and acetic acid in liquid samples were quantified by HPLC using an Aminex HPX87H Biorad column and an UV6000LP diode array detector. Total Organic Carbon (TOC) was measured on a Total Organic Carbon Analyzer 1020A from O.I. Analytical using the TC-IC method.

X-ray diffraction (XRD) patterns were obtained on a θ-θ Bruker D5005 diffractometer using Cu(Kα) radiation ($\lambda$ = 1.54186 Å) on the 20–60° $2\theta$ interval ($\Delta 2\theta$ = 0.06°; 2 s/step). BET specific surface areas (SSA) were determined via nitrogen adsorption at −196 °C on a Micromeritics Tristar 3000 apparatus after degassing at 250 °C for 120 min under vacuum. Support particle size ($d$) was calculated from XRD patterns using the Scherrer equation (Eq. (1) where $K$ = 0.9 is the Scherrer constant, $\lambda$ (m) is the X-ray wavelength and $\beta$ (rad) is the full width at half maximum corrected for instrumental broadening) and from SSA assuming quasi-crystalline spherical particles (Eq. (2) where $\rho$ (g $m^{-3}$) is the density of the oxide).

$$d_{XRD}(m) = \frac{K \cdot \lambda}{\beta \cdot \cos\ \theta} \tag{1}$$

$$d_{SSA}(m) = \frac{6 \cdot \rho}{SSA} \tag{2}$$

Oxygen Storage Capacity (OSC) values were measured at atmospheric pressure and 400 °C in a U-shaped reactor continuously purged with He. The sample (5 mg) was first saturated with oxygen and then purged for 10 min. OSC values were determined from the amount of $CO_2$ formed consecutively to CO injections under $CO/O_2$ alternate pulse conditions. In the case of supported metal catalysts, measured OSC values were corrected (Eq. (3)) to take account of the formation of surface PtO and bulk $RuO_2$ and their participation to CO consumption. The number of layers of oxygen atoms involved in the oxygen storage process (NL) was calculated from Eq. (4), where $OSC_{Surf}$ is the theoretical number of reducible surface