

# Application of $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ -supported noble metal catalysts in the catalytic wet air oxidation of 2-chlorophenol: Influence of the reaction conditions

Ning Li, Claude Descorme\*, Michèle Besson

*Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON), UMR 5256 CNRS/Université de Lyon,  
2 Avenue Albert Einstein, F-69626 Villeurbanne Cedex, France*

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## Abstract

A series of noble metal (Pt, Pd, Ru) loaded  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  catalysts were used in the Catalytic Wet Air Oxidation (CWAO) of 2-chlorophenol (2-CP) at relatively low temperature (393 K). Among the investigated noble metals, Ru exhibited the best activity. To optimize the reaction conditions, the effects of different parameters, such as the nature of the ruthenium precursor, the reaction temperature, the total pressure, the initial 2-CP concentration and the initial pH of the 2-CP solution on the catalytic performances of 3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  were evaluated. It was confirmed that the nature of the ruthenium precursor had nearly no effect on the activity of Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ . The activation energy for the 2-CP CWAO over Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  was calculated to be  $34 \text{ kJ mol}^{-1}$ . Unexpectedly, the 2-CP removal rate was 0.5 order with respect to the initial 2-CP concentration. Furthermore, the CWAO of 2-CP changed from first order (“oxygen diffusion control”) to zero order (“kinetic control”) with respect to the oxygen partial pressure, when the total pressure was higher than 4 MPa. The 2-CP conversion increased with the pH of the initial 2-CP solution. The dechlorination reaction is promoted at higher pH. However, too high pH hindered the total mineralization of 2-CP due to the possible poisoning effect of adsorbed carbonate and hydroxycarbonate species. The optimum initial pH was about 6.

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## 1. Introduction

Since the end of the 20th Century, with an increased awareness of the potential harmful effects of the hazardous organic substances present in many industrial wastewaters, the destruction of the toxic pollutants from the aqueous effluents has become mandatory [1–5]. Chlorophenols (CPs) are very important reactants and/or intermediates for the production of pesticides and dyes. Since most CPs are toxic, known or suspected endocrine disrupting compounds (EDCs), hardly biodegradable and very difficult to remove from the environment, they constitute a particular group of priority toxic pollutants listed by both the US EPA Clean Water Act and the European Decision 2455/2001/EC [1]. Therefore, the development of highly efficient techniques for the treatment of such organic-

contaminated wastewaters is crucial. Among the different techniques applied for the elimination of CPs, such as the photocatalytic degradation [6,7], the supercritical water oxidation [8], the Fenton process [9], the ozonation [10], the microwave irradiation enhanced advanced oxidation processes [11], the sonochemical degradation [12], etc., the wet air oxidation (WAO) is attracting more and more interest [13–21].

Generally, the WAO of organic compounds, in the absence of catalyst, was performed under high pressure (5–17.5 MPa) at high temperature (473–598 K) [22]. However, for the chlorinated organic compounds, serious corrosion problems might arise at such high temperature and high pressure, due to the production of HCl during the decomposition process. Then, it is preferable to operate at temperature and pressure as low as possible, even though low temperature and pressure are unfavorable for the effective degradation of the organic compounds in terms of reaction rate and reaction equilibrium. Consequently, some highly active catalysts must be found.

\* Corresponding author. Tel.: +33 4 7244 5307; fax: +33 4 7244 5399.

E-mail address: [claudedescorme@ircelyon.univ-lyon1.fr](mailto:claudedescorme@ircelyon.univ-lyon1.fr) (C. Descorme).

In the past years, several catalysts such as the activated carbons [16], CuSO<sub>4</sub>, MnO<sub>2</sub> or Co<sub>2</sub>O<sub>3</sub> [17], the noble metal loaded alumina, ceria, activated carbon, TiO<sub>2</sub> and ZrO<sub>2</sub> [18–20] and Cu loaded ceria [21] have been developed for the catalytic wet air oxidation (CWAO) of CPs. However, the operating temperature ( $\geq 413$  K) for all these catalysts was still relatively high.

In a recent work [23], a series of Ru loaded ceria-zirconia solid solution catalysts were used in the CWAO of 2-CP and exhibited higher activities than Ru/ZrO<sub>2</sub> and Ru/CeO<sub>2</sub>. Such advantage was even more pronounced in the presence of little amount of Pr or Nd. The most promising feature was their excellent performances at low temperature (393 K) and low total pressure (3 MPa). In this work, we studied further the activity of a series of noble metal (Pt, Pd, Ru) loaded Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> catalysts in the CWAO of 2-CP. The effects of various parameters such as the nature of the metal precursor, the reaction temperature, the total pressure, the initial 2-CP concentration and the initial pH on the activity of Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> were investigated in detail.

## 2. Experimental

### 2.1. Catalyst preparation

The Pt, Pd and Ru loaded catalysts were prepared as described previously [20,24,25]. The Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> support was supplied by Rhodia Electronics & Catalysis (La Rochelle, France). Pt, Pd, Ru were introduced on the support by incipient wetness impregnation, using aqueous solutions of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Aldrich), Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Aldrich), Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Alfa Aesar) or RuCl<sub>3</sub> (Aldrich) which concentrations were accurately determined by ICP-AES before impregnation. The metal loading was fixed at 3 wt.%. After the impregnation, the preparation was dried for 24 h at room temperature, introduced in a quartz tube cell and reduced in flowing hydrogen (15 L h<sup>-1</sup>) at 573 K for 2 h (temperature ramp rate: 1 K min<sup>-1</sup>). After cooling down to room temperature under H<sub>2</sub>, the cell was purged with argon and the catalyst was further passivated at room temperature under flowing 1% O<sub>2</sub>/N<sub>2</sub> (15 L h<sup>-1</sup>) for 2 h.

### 2.2. Characterizations

#### 2.2.1. Surface area

The catalysts specific surface areas were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 apparatus. Before each measurement, the samples were evacuated at 573 K for 3 h.

#### 2.2.2. XRD

XRD patterns were obtained on a Bruker D5005 diffractometer with an operating voltage of 40 kV and a current of 30 mA, using the Cu K $\alpha$  line (0.15406 nm) and a graphite monochromator. The angular range varied from 10° to 90°, with an increment of 0.02°. The average crystallite size was

estimated using the Debye–Scherrer equation:

$$D = \frac{0.90\lambda}{\beta \cos \theta}$$

where  $D$  is the crystallite size (nm),  $\lambda$  the excitation wavelength (nm),  $\beta$  the corrected full width at half maximum (rad) and  $\theta$  is the Bragg angle (rad).

#### 2.2.3. Infrared

FT-IR spectra were collected using a Vector 22 spectrometer (Bruker). The spectral resolution was set at 2 cm<sup>-1</sup> and 32 scans were accumulated. The samples were used without further pretreatment, mixed with KBr (dilution ca. 1:100), crushed and finally pelletized (pressure: 4 metric tons) before analysis under ambient conditions. Hereafter, we present the spectra acquired after reaction, after the spectra of the sample before reaction was subtracted and the baseline was corrected for scattering. These difference spectra are characteristic of the adsorbed species which are formed or consumed upon reaction.

### 2.3. Catalytic tests

Experiments were carried out in a 300 mL autoclave made of Hastelloy C22 (Model 4836, Parr Instrument Inc.). In a typical run, the autoclave was loaded with 150 mL 2-CP aqueous solution (2 g L<sup>-1</sup>, i.e. initial Total Organic Carbon (TOC) 1120 mg L<sup>-1</sup>). Based on preliminary studies we carried out in the case of the Ru/ZrO<sub>2</sub> catalyst to ensure the reaction is performed under kinetic control [20], the stirrer rotation speed was set at 1300 rpm and 0.5 g catalyst was used for each run. The reactor was first outgassed with argon (3 successive purges) before heating the reaction mixture to the desired reaction temperature under stirring. Then, the stirrer was stopped and air was admitted into the reactor until the predefined pressure was reached. A sample was subsequently withdrawn. The reaction finally started ( $t = 0$ ) when the stirrer was switched on. Liquid samples were periodically withdrawn from the reactor, centrifugated to remove any catalyst particle in the liquid sample and further analyzed.

The substrate and the reaction intermediates were analyzed using a HPLC system (Shimadzu) equipped with a UV–Vis detector set at 210 and 281 nm. A 250 mm  $\times$  4.6 mm C18 reverse phase column (Modulo-cart QS Uptisphere 5 MM1, Interchim) was used. The mobile phase was a mixture of 20 vol.% methanol and 80 vol.% water (flow rate: 1 mL min<sup>-1</sup>). The Total Organic Carbon (TOC) in the liquid sample was measured with a Shimadzu 5050 TOC analyzer and the pH was measured using a pH meter (Radiometer analytical PHM240).

## 3. Results and discussion

### 3.1. Characterizations

#### 3.1.1. Surface area

The BET surface areas of the different catalysts are listed in Table 1. The surface area of the Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> support is

Table 1  
Specific BET surface area of different solids

Samples	Surface area ( $\text{m}^2 \text{g}^{-1}$ )
$\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$	76.0
3 wt.% Pt/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$	79.1
3 wt.% Pd/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$	76.4
3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2^{\text{a}}$	75.9
3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2^{\text{b}}$	68.1

<sup>a</sup> Prepared from  $\text{Ru}(\text{NO})(\text{NO}_3)_3$ .

<sup>b</sup> Prepared from  $\text{RuCl}_3$ .

ca.  $76 \text{ m}^2 \text{ g}^{-1}$ . After the impregnation of the support with 3 wt.% of Pt, Pd or Ru, no significant change was observed compared to the bare support. Consequently, the porous structure of the oxide was not altered upon impregnation and reduction.

### 3.1.2. XRD

The XRD patterns of the different catalysts are shown in Fig. 1. The  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  support appeared as a true fluorite-type solid solution (cubic structure). According to the Debye–Scherrer equation, the average crystallite size was estimated as 8.1 nm. The corresponding geometrical surface area (external surface area) of the  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  support was approximated to be ca.  $115 \text{ m}^2 \text{ g}^{-1}$  (see Appendix A). By comparison with the oxide surface area measured by nitrogen adsorption at 77 K ( $76 \text{ m}^2 \text{ g}^{-1}$ ), one may conclude that (i) the oxide grains are mainly monocrystalline and/or that (ii) the crystallite size derived from the XRD pattern has been clearly underestimated using the Debye–Scherrer equation.

Furthermore, no change in the oxide structure and/or crystallite size was observed after impregnation with the different noble metals and reduction under  $\text{H}_2$  at 573 K. The 3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  catalysts prepared from either  $\text{RuCl}_3$  or  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  had similar XRD patterns which are similar to the pure  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  support. No diffraction

peak characteristic of the ruthenium phase could be observed, indicating that Ru is well dispersed on the support. On the opposite, in the case of the 3 wt.% Pt/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  and 3 wt.% Pd/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  catalysts, very weak peaks at ca.  $40^\circ$ , attributed to Pt (1 1 1) and Pd (1 1 1), respectively, could be detected. According to the Debye–Scherrer equation, the average Pt and Pd crystallite sizes were, respectively, estimated as 21.6 and 18.2 nm, which roughly correspond to 5% metal dispersion in both cases. Of course, the X-ray diffraction technique has some limitations since only the crystallites larger than 5 nm are detected. As a consequence, the dispersion might be underestimated. However, neither the hydrogen chemisorption nor the electron microscopy is directly applicable for the characterization of the  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}$ -supported catalysts. Upon hydrogen chemisorption, the support itself would also be responsible for part of the hydrogen uptake (spillover) and the metal dispersion could then be overestimated. Furthermore, in the case of ruthenium, the hydrogen chemisorption kinetics is very slow and the results are generally questionable. Regarding the electron microscopy direct observations, the contrast between the support and the metal particles is poor, essentially because these elements have quite similar atomic numbers. Any statistics to derive the particle size distribution is then hazardous. Another possibility would be to make replicas, but at that point no reliable methods could be developed to selectively dissolve the ceria-containing supports. Anyway, we are still confident in the fact that the Pt and Pd catalysts are more poorly dispersed than the Ru one, essentially because the incipient wetness impregnation is not the most appropriate method to disperse Pt or Pd.

### 3.2. Catalytic performances

As described in our previous work [20], the non-catalytic WAO of 2-CP is very slow. Even after 24 h reaction at 413 K and 5 MPa, the 2-CP conversion (34%) and the TOC removal (29%) are still very low. This result is consistent with earlier results reported in the literature [19,26].

#### 3.2.1. CWAO of 2-CP over pure and noble metal loaded $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$

Fig. 2 shows the evolution as a function of time of the 2-CP conversion, the TOC abatement and the pH value upon reaction at 393 K under 5 MPa total pressure over the bare  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  support and the Pt, Pd or Ru catalysts. Under such reaction conditions, the oxygen solubility was evaluated to be ca.  $0.20 \text{ g L}^{-1}$ . This value was extrapolated from the data published by Chang et al. [17]. As a pre-requisite, the oxygen partial pressure had to be derived from the total pressure in the reactor, depending on the reaction temperature. In first approximation, the perfect gas law was used and the water vapor pressure at a given temperature was extracted from the Handbook of Chemistry and Physics [27].

$\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  was only moderately active in the CWAO of 2-CP. Even after 24 h, the 2-CP conversion (61%) and the TOC removal (56%) were still limited. After impregnation of the support with 3 wt.% Pt, Pd or Ru, the

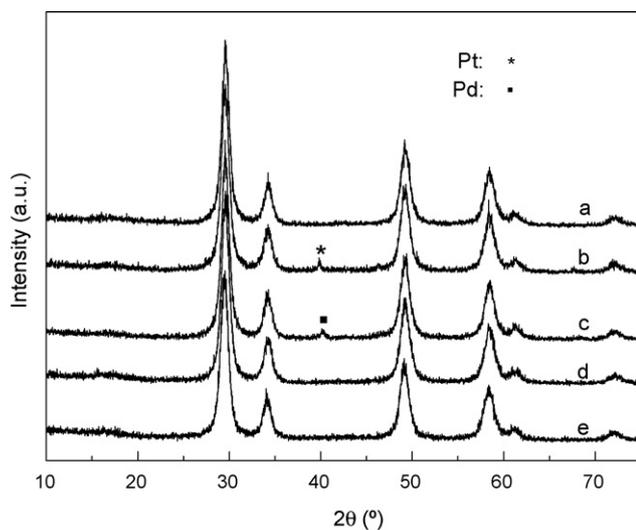


Fig. 1. XRD patterns of  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (a), 3 wt.% Pt/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (b), 3 wt.% Pd/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (c), 3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  ex.  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (d), and 3 wt.% Ru/ $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  ex.  $\text{RuCl}_3$  (e).

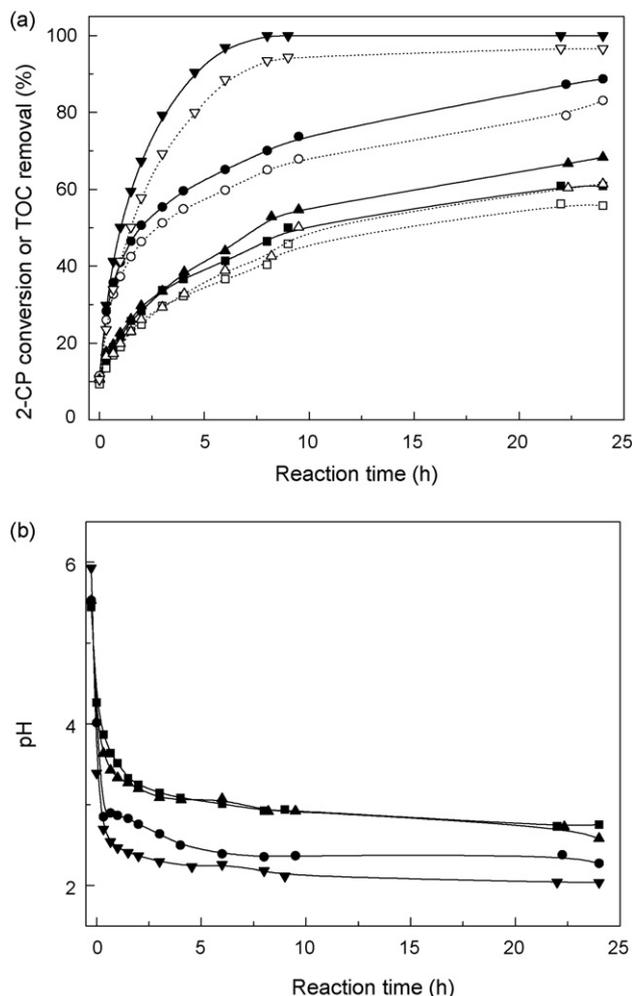


Fig. 2. Evolution of the 2-CP conversion (a, full symbols, solid lines), the TOC removal (a, open symbols, dotted lines) and pH (b) in the catalytic wet air oxidation (CWAO) of 2-CP over Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (■, □), 3 wt.% Pt/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (●, ○), 3 wt.% Pd/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (▲, △), and 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (▼, ▽) [0.5 g catalyst, 393 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

catalytic performances of the solids were improved to a different extent depending on the noble metal. Ruthenium had the largest effect: after 8 h reaction only, the 2-CP conversion was complete and the TOC removal reached 94%. The activity sequence would be: Ru > Pt ≫ Pd ≈ pure support. The initial 2-CP removal rates over pure and Pt, Pd, Ru loaded Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> were calculated to be ca. 0.7, 1.7, 0.6, 2.2 mmol<sub>2-CP</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>.

However, it is noteworthy that the preparation method was not optimized for the palladium and platinum supported catalysts and, as a result, the metal dispersion was different from one metal to the other. In fact, taking into account (i) the metal atomic concentration based on the molecular weight of the different metals ( $M_{\text{Ru}} = 101.1 \text{ g mol}^{-1}$ ,  $M_{\text{Pd}} = 106.4 \text{ g mol}^{-1}$ ,  $M_{\text{Pt}} = 195.1 \text{ g mol}^{-1}$ ) and (ii) the metallic phase dispersion derived from the XRD analysis, even though it might be questionable, the initial activity of the Pt catalyst, expressed per square meter of metal exposed to the reactants, would be much higher than the one of the Ru catalyst. Anyway, Pt appeared to be

much less efficient in the degradation of 2-CP and carboxylic acids which are formed upon the degradation of the 2-CP molecule, as shown by the rapid slow down of the 2-CP conversion and TOC abatement rates. After 8 h reaction, the 2-CP conversion was 70% and the TOC abatement reached 63%, only. Therefore, in the following, we concentrated on Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub>.

Furthermore, as proposed earlier, the initial adsorption of the 2-CP molecule on the different support can be accessed from the TOC removal at  $t = 0$  [20]. From Fig. 2a, one might see that the TOC abatement at zero time over the pure and the different noble metal loaded Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> catalysts is very similar (between 9 and 11%). Such observation tends to indicate that (i) the 2-CP molecules mainly adsorb on the support, (ii) the adsorption of the 2-CP molecule on the Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> support is not altered by the presence of the metallic particles and (iii) the initial adsorption of the 2-CP molecule on the catalyst surface is not a key parameter controlling the overall catalyst activity.

Moreover, the initial pH of the 2-CP solution was around 6 (Fig. 2b). At the very beginning of the reaction, the pH decreases sharply. As shown earlier, the increase of the acidity is directly connected with the degradation of the 2-CP molecule and the production of HCl (2-CP dechlorination) [19,20]. The formation of acidic reaction intermediates also contributes to such acidification to a lower extent. Indeed, from the reaction mixture analysis, small chain carboxylic acids such as acetic, chloroacetic and succinic acids could be identified, indicating that ring cleavage occurs upon the degradation of the 2-CP molecule. The fastest decrease is observed when Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> is used as a catalyst, indicating a deeper oxidation. Consequently, a rapid measure of the pH could already give approximate information about the degradation degree of the 2-CP molecule.

As reported in the literature [18–20], we also confirmed the production of trace amounts of aromatic intermediates such as catechol, chlorohydroquinone, hydroquinone, chloro-*p*-benzoquinone and benzoquinone upon 2-CP conversion, essentially at the very initial reaction time. Such observation would indicate the progressive oxidation of the aromatic ring before ring opening occurs. Whatever the catalyst, at a given conversion, no significant difference in the by-products distribution could be observed.

Furthermore, by comparing the initial 2-CP conversion and TOC abatement rates, both expressed in g<sub>C</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup> (not given), it is observed that almost 80% of the 2-CP molecules are directly mineralized (see Fig. 2a for direct visualization).

Finally, the samples were tentatively characterized by infrared after reaction at 393 K under 5 MPa total pressure. The spectra appeared to be quite complex, especially in the 1800–1000 cm<sup>-1</sup> spectral domain since C–O, O–C–O, O–H and C–H vibrations might be simultaneously detected. The spectra are presented in Fig. 3. These spectra were quite different from those recently published by Mikulová et al. [28–30]. Nevertheless, these Authors somehow proposed the same attributions as we do. Mainly bidentate (1600, 1310 cm<sup>-1</sup>) and monodentate (1530, 1350 cm<sup>-1</sup>) carbonates and hydrogen carbo-

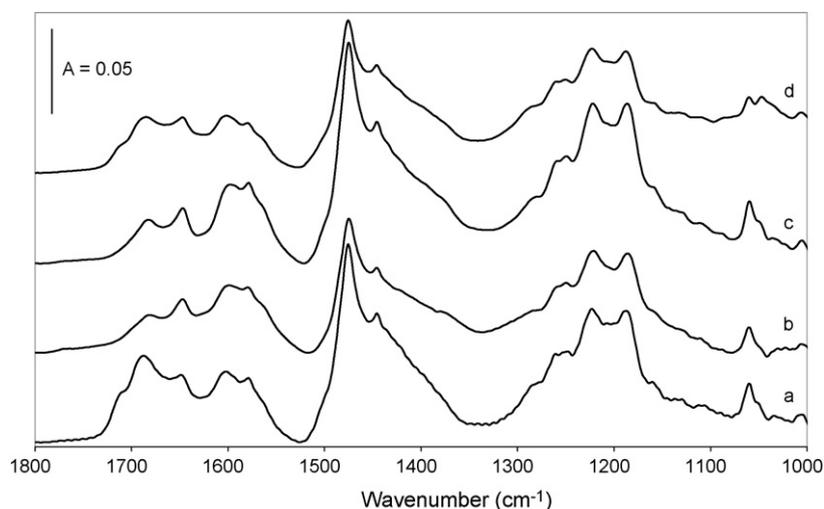


Fig. 3. FT-IR spectra of  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (a), 3 wt.%  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (b), 3 wt.%  $\text{Pt}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (c) and 3 wt.%  $\text{Pd}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  (d) after reaction at 393 K, 5 MPa. The spectra of the sample before reaction was first subtracted before the baseline was corrected for scattering.

nates ( $1630, 1400\text{ cm}^{-1}$ ) were identified by these Authors. In the present study, the main bands were characteristic of adsorbed bidentate (ca.  $1577$  and  $1059\text{ cm}^{-1}$ ) and polydentate (ca.  $1474, 1400$  (diffuse) and  $1059\text{ cm}^{-1}$ ) carbonate and hydrogen carbonate (ca.  $1594, 1444, 1247$  and  $1059\text{ cm}^{-1}$ ) species. These attributions were based on a literature survey [31–41] on the characterization by infrared of the carbonate, formate, hydrogenocarbonate, inorganic carboxylate, oxalate, carboxylic acid and carbonite species possibly formed at the surface of ceria and ceria-zirconia oxides (Table 2). The platinum catalyst showed the highest surface coverage by carbonates and hydrogen carbonates, while the ruthenium catalyst exhibited a cleaner surface. This observation could explain (i) the rapid deactivation of  $\text{Pt}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  and (ii) the good performances of  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ . Additional bands at ca.  $1685$  and  $1645\text{ cm}^{-1}$  were quite unambiguously attributed to adsorbed carboxylic acids (unconverted reaction intermediates) and water, respectively. The highest concentration in adsorbed unconverted carboxylic acids was found in the case of the bare support, as an additional indication of the poor activity of the support alone for the oxidation of intermediates derived from ring cleavage.

### 3.2.2. Effect of the nature of the Ru precursor on the activity of $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ in the CWAO of 2-CP

It was found earlier that the nature of the ruthenium precursor had a clear effect on the activity of  $\text{Ru}/\text{ZrO}_2$  in the CWAO of 2-CP [20] and *p*-hydroxybenzoic acid [25]. The  $\text{Ru}/\text{ZrO}_2$  catalyst prepared from  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  was more efficient than the corresponding catalyst prepared from  $\text{RuCl}_3$ . In this work, we also investigated the effect of the nature of the Ru precursor ( $\text{RuCl}_3$  vs.  $\text{Ru}(\text{NO})(\text{NO}_3)_3$ ) on the catalytic performances of 3 wt.%  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ . Whatever the Ru precursor, the 2-CP conversion, the TOC abatement and the pH evolution were very close (not shown). Consequently, the  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  precursor will be used for the following catalysts' preparation.

### 3.2.3. Effect of the reaction temperature on the activity of $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$ in the CWAO of 2-CP

The influence of the reaction temperature was studied under 5 MPa total pressure in the range 383–413 K. The oxygen solubility was calculated to be 0.18, 0.20, 0.23 and  $0.25\text{ g L}^{-1}$  at 383, 393, 403 and 413 K, respectively.

Table 2

IR bands characteristic of carbonate, formate, hydrogenocarbonate, inorganic carboxylate, carboxylic acid and carbonite species at the surface of ceria and ceria-zirconia supports [30–40]

Name	Literature data
Monodentate carbonate	1454–1520, 1325–1358, 1045–1085, 854–856
Bidentate carbonate	1546–1588, 1286–1320, 1009–1063, 850–872
Bridged carbonate	1728–1806, 1393–1396, 1219–1232, 1132–1150
Polydentate carbonate	1405–1508, 1348–1390, 1040–1115, 854–884
Formate	2875–2947, 2840–2848, 1545–1600, 1372–1383, 1307–1373, 790
Hydrogen carbonate	3608–3619, 1592–1613, 1390–1450, 1025–1063, 1218–1225, 823–861
Inorganic carboxylates	1506–1514, 1560, 1310–1316
Adsorbed carboxylic acids	1600–1700, 1335

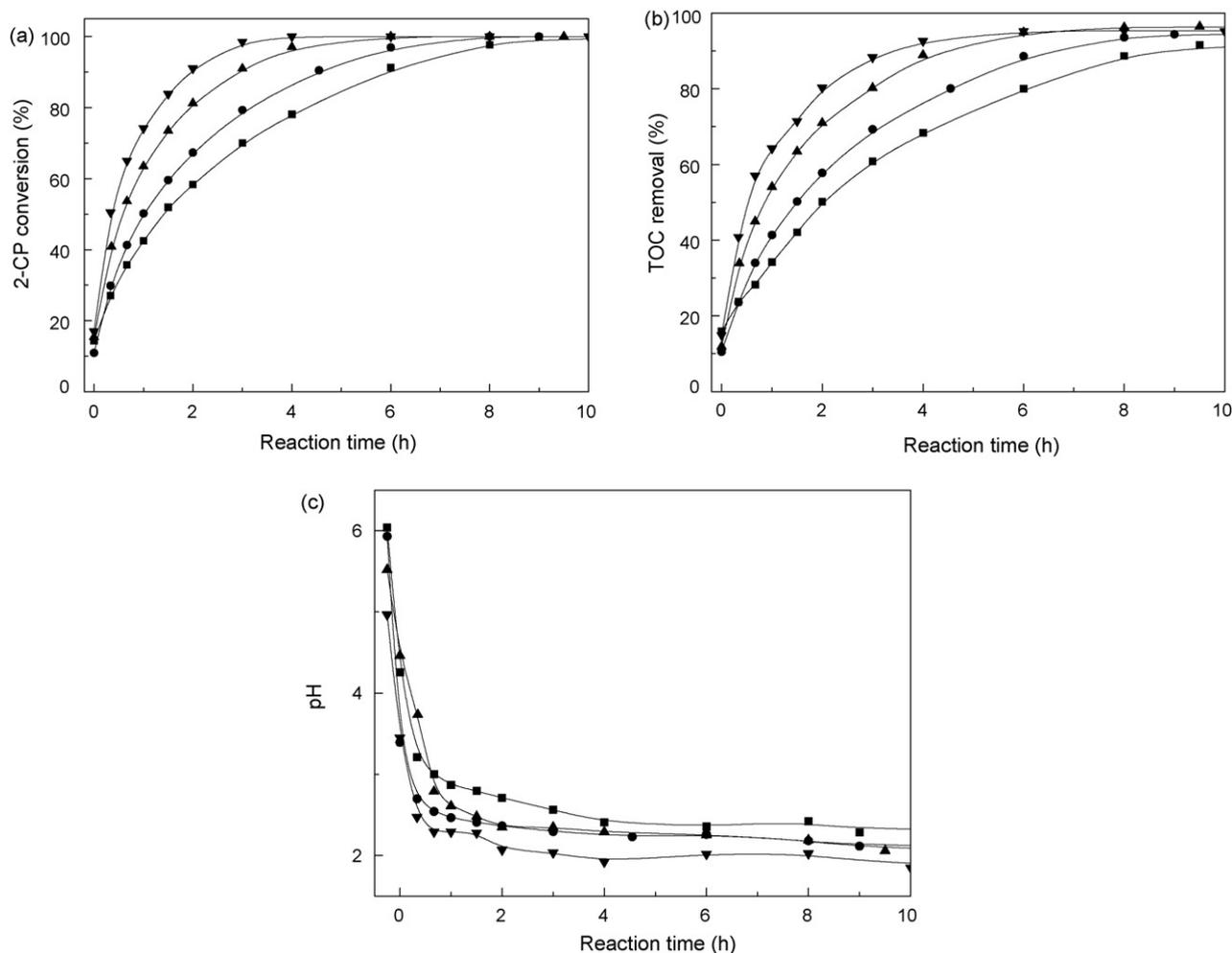


Fig. 4. Evolution of the 2-CP conversion (a), the TOC removal (b) and pH (c) in the catalytic wet air oxidation (CWAO) of 2-CP over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) at 383 K (■), 393 K (●), 403 K (▲) and 413 K (▼) [0.5 g catalyst, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

Fig. 4 shows the evolution of the 2-CP conversion, the TOC removal and the pH upon time on stream over the 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> ex. Ru(NO)(NO<sub>3</sub>)<sub>3</sub> catalyst at different temperatures. Just as we observed on Ru/ZrO<sub>2</sub> [20], both the 2-CP conversion and the TOC removal increased with temperature. As a direct result, the pH of the reaction mixture also decreased faster at higher temperature. It is clear that higher temperatures favor the CWAO of 2-CP. However, higher temperatures practically translate into higher operating costs and severe corrosion problems due to the presence of HCl generated during the reaction, as demonstrated by Kojima et al. [19]. Additionally, from a fundamental point of view, one has to make sure that the reaction is operated under chemical control, that is, not too fast. Furthermore, in order to observe the possible effect of the other operating parameters, the reaction should not be too fast either. Taking into consideration the above mentioned multisided reasons, we considered 393 K as the optimum temperature for the subsequent study of the CWAO of 2-CP over the Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> catalyst.

From the Arrhenius plot ( $\ln r_{0(2-CP)}$  vs.  $1/T$ ) for the evolution of the initial 2-CP conversion rate as a function of temperature (not shown), the apparent activation energy for the CWAO of 2-

CP over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> was calculated to be 34 kJ mol<sup>-1</sup>. Such value is clearly lower than the value reported by Joglekar et al. in the non-catalytic WAO of 2-CP (145 kJ mol<sup>-1</sup> upon steady state operation) [26] but very close to what could be observed in the CWAO of 2-CP over Ru/ZrO<sub>2</sub> (36 kJ mol<sup>-1</sup>) [20] and in the CWAO of phenol over Pt-Ru/C (34 kJ mol<sup>-1</sup>) [42].

Finally, looking at the mineralization efficiency as a function of temperature, by comparing the initial 2-CP conversion and TOC abatement rates ( $g_C g_{catalyst}^{-1} h^{-1}$ ), it is observed that ca. 80% of the 2-CP molecules are directly mineralized, except at the lowest temperature (383 K) where less than 60% mineralization was directly achieved. Mineralization is clearly limiting at low temperature.

### 3.2.4. Effect of the total pressure on the activity of Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> in the CWAO of 2-CP

It has been found earlier that the oxygen partial pressure has some impact on both the conversion and the mineralization of the organic contaminants upon CWAO [20,43–45]. This effect might be related to the amount of oxygen which is available to the active site.

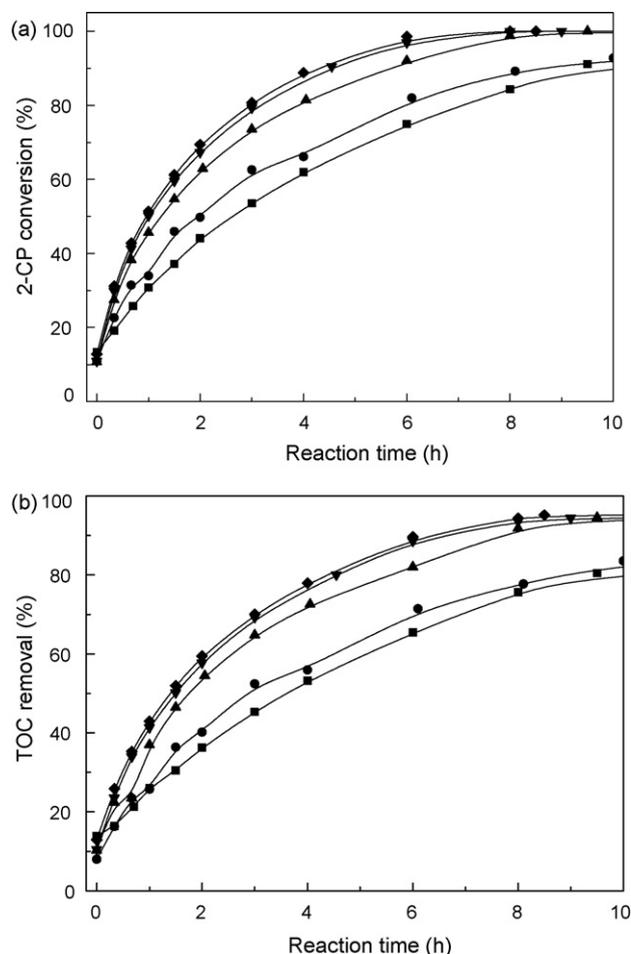


Fig. 5. Evolution of the 2-CP conversion (a) and the TOC removal (b) in the catalytic wet air oxidation (CWAO) of 2-CP over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) at 2 MPa (■), 3 MPa (●), 4 MPa (▲), 5 MPa (▼) and 6 MPa (◆) [0.5 g catalyst, 393 K, 1300 rpm [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

We investigated the effect of the total pressure (2–6 MPa) at 393 K using the 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub>, ex. Ru(NO)(NO<sub>3</sub>)<sub>3</sub> catalyst. 2 MPa total pressure was the minimum pressure required for the complete oxidation of 2-CP to CO<sub>2</sub> and H<sub>2</sub>O under our reaction conditions. Under such reaction conditions, the oxygen solubility was approximated to be 0.08, 0.12, 0.16, 0.20 and 0.25 g L<sup>-1</sup> under 2, 3, 4, 5 and 6 MPa, respectively.

As shown in Fig. 5, the 2-CP conversion and the TOC abatement improved as the total pressure increased. This effect was evident when the total pressure increased from 2 to 4 MPa, while the difference between 4 and 6 MPa was somehow negligible. Above 4 MPa, the 2-CP conversion is zero order with respect to the oxygen pressure. The oxygen diffusion to the catalyst surface is not limiting anymore for the reaction and the 2-CP CWAO transforms from oxygen diffusion-controlled to kinetic-controlled. These results are similar to what we found in the CWAO of 2-CP over Ru/ZrO<sub>2</sub> [20] and what Joglekar et al. found in the WAO of phenol and 2-CP, in the absence of any catalyst [26].

Finally, the degree of mineralization of the organic compounds, derived from the ratio of the initial TOC abatement

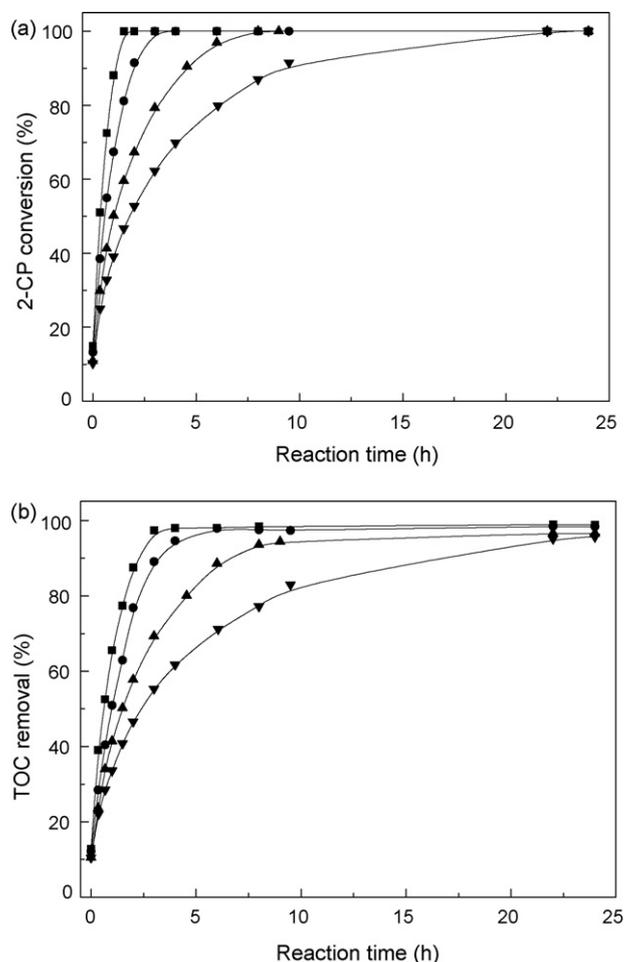


Fig. 6. Evolution of the 2-CP conversion (a) and the TOC removal (b) in the catalytic wet air oxidation (CWAO) of 2-CP over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) [0.5 g catalyst, 393 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 0.5 g L<sup>-1</sup> (■), 1 g L<sup>-1</sup> (●), 2 g L<sup>-1</sup> (▲), 3 g L<sup>-1</sup> (▼)].

rate to the initial 2-CP conversion rate, both expressed in  $\text{g}_C \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ , was almost independent of the oxygen partial pressure/solubility (ca. 80%). Such observation confirms that the oxygen transfer from the gas to the liquid phase and from the liquid phase up to the catalyst surface is not rate limiting.

### 3.2.5. Effect of the initial 2-CP concentration on the activity of Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> in the CWAO of 2-CP

Fig. 6 shows the results obtained upon the CWAO of 2-CP solutions (0.5–3 g L<sup>-1</sup>) over the 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub>, ex. Ru(NO)(NO<sub>3</sub>)<sub>3</sub> catalyst, at 393 K and 5 MPa total pressure. The initial rates for the 2-CP degradation ( $r_{0(2-CP)}$ ) and the TOC abatement increased with the initial 2-CP concentration. We found that the reaction order is about 0.5 with respect to the initial 2-CP concentration. This result is markedly different from what we observed on Ru/ZrO<sub>2</sub> where the reaction was zero order with respect to the initial 2-CP concentration [20]. In the present case, the reaction is somehow controlled by the adsorption of the 2-CP molecule since the catalyst surface is not fully saturated with the 2-CP molecule.

Such differences could be explained by the different adsorption properties of the two supports. Indeed, whatever

Table 3  
Initial rates for 2-CP conversion and TOC abatement, mineralization degree (%) and time to reach 80% TOC abatement (h) at different initial pH

Initial pH of 2-CP solution	2.1	6.0	9.1	10.4	12.0
Initial 2-CP conversion rate ( $\text{mmol}_{2\text{-CP}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ )	0.9	2.2	5.1	5.3	5.4
Initial 2-CP conversion rate ( $\text{g}_{\text{C}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ )	0.07	0.16	0.37	0.38	0.39
Initial TOC abatement rate ( $\text{g}_{\text{C}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ )	0.05	0.12	0.20	0.21	0.18
Mineralization degree (ratio of the Initial 2-CP conversion rate to the Initial TOC abatement rate) (%)	71	75	54	55	46
Time to reach 80% TOC removal (h)	11.3	4.5	5.8	6.7	9.5

[0.5 g 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) catalyst, 393 K, 5 MPa, 1300 rpm].

the initial 2-CP concentration, the initial TOC abatement level over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> was ca. 10–13%, indicating that the catalyst surface was never saturated with the 2-CP molecules, at least up to 3 g L<sup>-1</sup> 2-CP, even though the surface area of the Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> support is smaller compared to the ZrO<sub>2</sub> support. In the case of Ru/ZrO<sub>2</sub> [20], the adsorption reached a plateau above 1 g L<sup>-1</sup> 2-CP and the 2-CP adsorption could be simply described through the Langmuir–Hinshelwood equation.

### 3.2.6. Effect of the initial pH value of the 2-CP solution on the activity of Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> in the CWAO of 2-CP

The effect of pH on the efficiency and selectivity of the oxidation process was studied with the objective to find the optimum conditions for the complete transformation of 2-CP to harmless products (H<sub>2</sub>O, CO<sub>2</sub>). Experiments were carried out with a 2 g L<sup>-1</sup> 2-CP solution with initial pH in the range 2–12. Reactions were performed using 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>

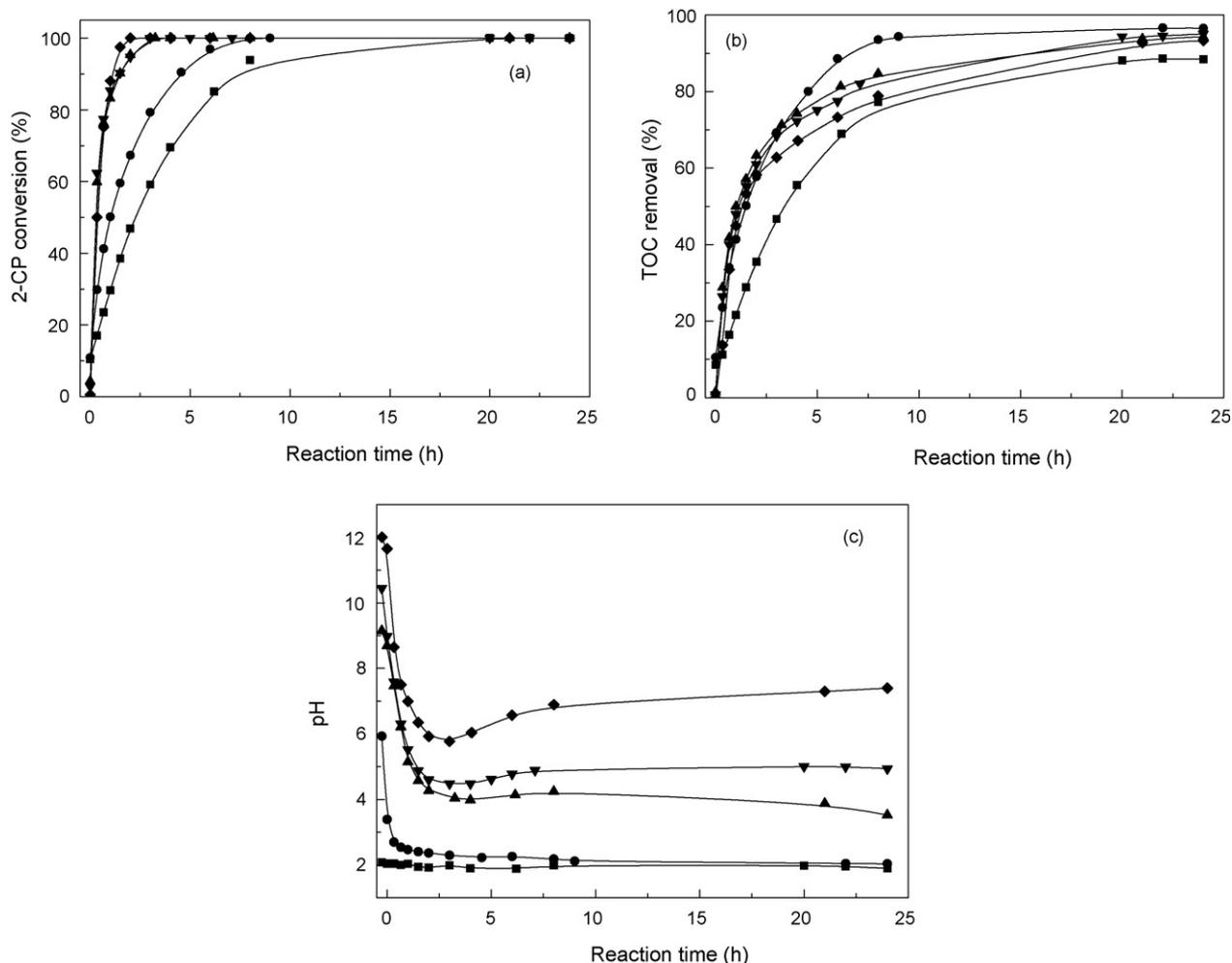


Fig. 7. Evolution of the 2-CP conversion (a), the TOC removal (b) and pH (c) in the catalytic wet air oxidation (CWAO) of 2-CP over 3 wt.% Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) [0.5 g catalyst, 393 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>, initial pH 2.1 (■), 6.0 (●), 9.1 (▲), 10.4 (▼), 12.0 (◆)].

$\text{Pr}_{0.04}\text{O}_2$ , ex.  $\text{Ru}(\text{NO})(\text{NO}_3)_3$ , at 393 K under 5 MPa total pressure. Either  $\text{H}_3\text{PO}_4$  or  $\text{NaOH}$  was used to adjust the initial pH to the desired value.

The results are presented in Fig. 7 and summarized in Table 3. The initial 2-CP conversion rate first increases as the pH increases from 2 to 9 and then reaches a plateau above pH 9. Nevertheless, looking at the overall 2-CP conversion, the higher the pH, the shorter the reaction time required to achieve 100% 2-CP conversion. On the opposite, the mineralization process was most efficient at pH 6, since 94% of the initial chlorophenol could be mineralized in less than 10 h. These results are quite similar to what we found on  $\text{Ru}/\text{ZrO}_2$  [20] and what Kojima et al. presented earlier in the case of  $\text{Ru}/\text{TiO}_2$  [19]. One possible explanation could be the conflict that somehow exists between the dechlorination reaction of the 2-CP molecule on one side and the mineralization of the reaction intermediates on the other side. However, in this case, hindering effects resulting from electrostatic barriers between the catalyst surface and the reaction intermediates could not justify the mineralization limitations, as in the case of  $\text{Ru}/\text{ZrO}_2$  [20] and  $\text{Ru}/\text{TiO}_2$  [19]. In fact, there must be something specific to the  $\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  mixed oxide support. Recently, Mikulová et al. investigated the CWAO of acetic acid over Pt and Ru loaded  $\text{CeO}_2$  catalysts [28–30]. The formation of carbonate species at the catalyst surface, especially at the metal/support interface, was proposed to explain the catalyst inhibition. In our case, we also noticed that the inorganic carbon (IC) concentration in the reaction mixture increased when the initial pH was higher, indicating that more carbonates ( $\text{p}K_a = 10.3$ ) and/or bicarbonates ( $\text{p}K_a = 6.4$ ) were present in the solution. These surface species could easily adsorb on the positively charged catalyst surface, hinder the subsequent adsorption of the organic compounds and prevent the further conversion of these reaction intermediates.

Furthermore, all liquid samples were analyzed by HPLC but no qualitative difference was observed in the sample composition whatever the initial pH. Indeed, as far as ca. 70% of the initial 2-chlorophenol is directly mineralized, the concentration in the different reaction intermediates is very low and we clearly faced some sensitivity limitations using HPLC. LC–MS analysis were also performed at Service Central d'Analyse du CNRS (Solaize, France) to identify some of the reaction intermediates, without success.

Looking at the evolution of the initial TOC abatement rate as a function of the initial pH and comparing it with the evolution of the initial 2-CP conversion rate (Table 3), it is observed that the mineralization efficiency of the catalyst strongly decreases for pH higher than 8, from ca. 70% down to ca. 50%.

Moreover, the TOC removal at zero time for pH 2.1, 6.0, 9.1, 10.4, 12.0, which represents the amount of 2-CP which is initially adsorbed on the catalyst surface, was ca. 9, 11, 1.4, 0.8 and 0%, respectively. The 2-CP adsorption reached a maximum when the initial pH was about 6.0. This result is similar to what we found on  $\text{Ru}/\text{ZrO}_2$  [20] and indicates that the 2-CP molecule is more likely to adsorb under neutral or acidic conditions.

Furthermore, when the initial pH is higher than 9, the pH of the solution first decreases and then increases at the end of the reaction. This result is similar to what we observed in the CWAO of 2-CP over  $\text{Ru}/\text{ZrO}_2$  [20] and can be explained by the deeper oxidation of the organic acids to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This trend for the evolution of the pH as a function of time is even more pronounced when the initial pH is 12.0. However, when the initial pH of the solution is 10.4 and 12.0, the minimum pH upon reaction is 4.5 and 5.7, respectively, and the final pH of the solution is about 5.0 and 7.4, respectively.

Finally, the  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  catalysts were characterized by infrared after reaction at different initial pH (393 K, 5 MPa total pressure). The spectra appeared to be quite complex, as previously mentioned, but no significant difference was observed as a function of the initial pH (not shown). Mainly adsorbed bidentate and polydentate carbonate and hydrogen carbonate species could be identified. Such observation might not be so surprising as far as the catalysts were analyzed at the very end of the reaction and, at that point, the 2-CP conversion was 100% in all cases and the TOC abatement was quite similar whatever the initial pH (88–96%).

Anyway, pH 6, which is the natural pH of the 2-CP solution we used ( $2 \text{ g L}^{-1}$ ), was considered as the optimum. Such result might be interesting from a practical point of view as far as no acid or base addition would be required before the CWAO treatment.

### 3.3. Catalyst stability

The catalyst stability is of primary importance, especially regarding industrial applications as well as potential toxicity issues if any components of the catalyst would be leached out.

For that reason, the “short” term (few tens of hours) stability of the  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}$  catalyst was evaluated. We could observe first that the  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}$  catalyst does not lose any of its activity upon recycling experiments performed in the batch reactor (not shown). Furthermore, the chemical stability of the catalyst was checked. For that, the Ru concentration in the liquid phase after 24 h reaction was repeatedly measured by ICP-OES (Activa, Horiba Jobin Yvon). As earlier reported in the CWAO of 2-CP on  $\text{Ru}/\text{ZrO}_2$  [20], no Ru could be detected at the detection limit of the equipment we used (0.5 ppm).

However, to really probe the stability of the  $\text{Ru}/\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2$  catalyst, “long” term experiments in a continuous trickle-bed reactor should be performed. In that case, shaped materials (beads, extrudates ...) are absolutely required. Unfortunately, to the Authors' knowledge, ceria-based materials are only available as powders. Furthermore, binders are frequently used to produce shaped materials and such binders might not be stable under the applied hydrothermal conditions. Consequently, we did not have any chance to carry out such study. Nevertheless, it was clearly shown earlier in the case of  $\text{Ru}/\text{TiO}_2$  and  $\text{Ru}/\text{ZrO}_2$  [4,46–48] that Ru catalysts are very stable under the applied reaction conditions, even upon continuous operation for more than one thousand of hours in the CWAO of real industrial effluents.

#### 4. Conclusions

It was demonstrated that Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> is an efficient catalyst for the CWAO of 2-CP. High 2-CP conversion and TOC removal could be achieved at relatively low reaction temperature and moderate pressure. The activation energy for the CWAO of 2-CP over Ru/Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> was calculated to be 34 kJ mol<sup>-1</sup>, indicating clearly the advantage of the CWAO process over the thermal process.

Above 4 MPa, the 2-CP CWAO was shown to be zero order with respect to the oxygen partial pressure. Additionally, the 2-CP removal rate is 0.5 order with respect to the initial 2-CP concentration, indicating that the adsorption of the 2-CP molecules somehow controls the reaction kinetics.

Finally, high initial pH favored the 2-CP conversion by accelerating the dechlorination reaction. However, too high pH also hindered the total mineralization of the 2-CP molecule since the adsorption of carbonates and bicarbonates produced upon reaction was shown to hinder the reaction. In order to achieve the maximum conversion and mineralization of the 2-CP molecules, the optimum for the initial pH of the 2-CP solution was shown to be pH 6.

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#### Appendix A

Assuming the oxide grains to be spherical, the following relationship between the particle size ( $d$  in Å) and the external surface area ( $S_{\text{ext}}$  in m<sup>2</sup> g<sup>-1</sup>) might be derived:

$$S_{\text{ext}} = \frac{60,000}{\rho \times d} \quad (1)$$

where  $\rho$  is the mixed oxide density (cm<sup>3</sup> g<sup>-1</sup>), which might be approximated considering the mixed oxide density to be the sum of the single oxide densities ( $\rho_i$ ), normalized to the weight fraction ( $x_i$ ) for each of them:

$$\rho = \sum x_i \rho_i \quad \text{with} \quad \sum x_i = 1 \quad (2)$$

In the case of the Ce<sub>0.33</sub>Zr<sub>0.63</sub>Pr<sub>0.04</sub>O<sub>2</sub> support, we obtain:

$$\begin{aligned} \rho_{\text{Ce}_{0.33}\text{Zr}_{0.63}\text{Pr}_{0.04}\text{O}_2} &\cong (0.40 \times \rho_{\text{CeO}_2}) + (0.55 \times \rho_{\text{ZrO}_2}) \\ &+ (0.05 \times \rho_{\text{Pr}_2\text{O}_3}) \cong 6.433 \end{aligned} \quad (3)$$

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