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# Catalytic wet air oxidation of aqueous solution of 2-chlorophenol over Ru/zirconia catalysts

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Ru loaded zirconia catalysts (Ru/ZrO<sub>2</sub>) were found to be active in the catalytic wet air oxidation (CWAO) of 2-chlorophenol (2-CP) at relatively mild temperature. To optimize the reaction conditions, the effects of different operating parameters, such as the rotation speed, the reaction temperature, the total pressure, the initial concentration and the pH of the initial 2-CP solution on the catalytic activity of 3 wt.% Ru/ZrO<sub>2</sub> were evaluated. The activation energy for the CWAO of 2-CP over Ru/ZrO<sub>2</sub> was calculated to be 36 kJ mol<sup>-1</sup>. The 2-CP removal rate is zero order with respect to the initial 2-CP concentration. The CWAO of 2-CP changes from first order (oxygen diffusion control) to zero order (kinetic control) with respect to the oxygen partial pressure when the total pressure is higher than 4 MPa. The conversion of 2-CP increases with the pH of the initial 2-CP solution. The dechlorination reaction is promoted at higher pH. However, too high pH limits the total mineralization of 2-CP because the adsorption of the reaction intermediates is hindered. It was also confirmed that Ru(NO)(NO<sub>3</sub>)<sub>3</sub> is better than RuCl<sub>3</sub> to act as a ruthenium precursor.

**Keywords:** Catalytic wet air oxidation (CWAO); Chlorophenol; Ru; Zirconia

## 1. Introduction

From the beginning of the 21st century, with an increasing social and political concern on the environment, the removal of toxic organic compounds from aqueous wastewater has drawn a lot of attention [1–5]. Chlorophenols (CPs) are very important chemical compounds and intermediates in several chemical industries, such as the production of pesticides and dyes. Because most CPs are toxic, hardly biodegradable and very difficult to remove from the environment, they constitute a particular group of priority toxic pollutants listed in both the US EPA Clean Water Act and the European Decision 2455/2001/EC [1]. Therefore, to protect the environment, it is necessary to develop some highly efficient techniques for the treatment of such organic-contaminated wastewater. 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 [11], the sonochemical degradation [12],

etc., the wet air oxidation (WAO) is attracting more and more interest [13–20]. Using such a process, chlorinated organic contaminants might be totally mineralized by oxygen to CO<sub>2</sub>, H<sub>2</sub>O and HCl, with relatively low energy consumption.

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) [21]. However, for the chlorinated organic compounds, serious corrosion problems might arise at such high temperature and pressure, due to the HCl, which is produced 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 organic compounds in terms of reaction rate and reaction equilibrium. To solve this problem, some highly active catalysts must be found. In the past years, several catalysts have been developed for the catalytic wet air oxidation (CWAO) of chlorophenols. For example, Chang et al. [17] compared the activities of CuSO<sub>4</sub>, MnO<sub>2</sub> and Co<sub>2</sub>O<sub>3</sub> in the CWAO of 4-CP in the temperature range 423–473 K. It was found that CuSO<sub>4</sub> is the most effective catalyst and that alkaline conditions favor the degradation of 4-CP. Qin et al. [18] investigated the activities of Pt, Pd and Ru loaded alumina, ceria and activated carbon catalysts in the CWAO of

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4-CP at 453 K. Activated-carbon-supported catalysts were found to be the most active. Posada et al. [19] also studied the CWA of 2-CP over Cu loaded ceria catalysts at 433 K. It was suggested that the high activity of the copper-ceria catalysts is related to the modification of the structural and redox properties of the cerium oxide upon copper addition. However, the operating temperature for these catalysts was relatively high. Recently, Kojima et al. [20] found that Ru loaded  $\text{TiO}_2$  catalyst was active for the CWA of 2-CP. Over this kind of catalyst, 2-CP could be completely removed at relatively mild temperature (413 K). Suarez-Ojeda et al. [16] used activated carbon as the catalyst for the CWA of 2-CP with a trickle bed system and got about 55% 2-CP conversion and 50% TOC removal at 413 K. However, it is still necessary to find some highly efficient catalysts operating at lower temperature. In previous works in our group, Ru loaded zirconia ( $\text{Ru/ZrO}_2$ ) catalysts were proved to be active for the wet air oxidation of Kraft bleaching plant effluents [22], *p*-hydroxybenzoic acid [23], acetic acid [24], succinic acid [23,24] and *p*-coumaric acid [25]. In this work, we studied the catalytic performances of  $\text{Ru/ZrO}_2$  for the CWA of 2-CP. To optimize the catalyst performances, the effects of various parameters, such as the rotation speed, the ruthenium precursor, the reaction temperature, the total pressure, the initial concentration and the initial pH were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The Ru loaded zirconia catalyst was prepared as described previously [25]. The  $\text{ZrO}_2$  support was supplied by Melcat (XZ0 923/01, BET surface area  $90 \text{ m}^2 \text{ g}^{-1}$ , particle size 15–20  $\mu\text{m}$ ). Ru was introduced by incipient wetness impregnation using aqueous solutions of  $\text{Ru(NO)(NO}_3)_3$  (Alfa Aesar) or  $\text{RuCl}_3$  (Aldrich), which concentrations were accurately determined by ICP-AES before impregnation. After the impregnation, the preparation was dried for 24 h at room temperature, introduced in a quartz tube cell, reduced in flowing hydrogen ( $15 \text{ L h}^{-1}$ ) at 573 K for 2 h (temperature ramp rate:  $1 \text{ K min}^{-1}$ ). After cooling down to room temperature under  $\text{H}_2$ , the cell was purged with argon and the catalyst was further passivated at room temperature under flowing 1%  $\text{O}_2/\text{N}_2$  ( $15 \text{ L h}^{-1}$ ) for 2 h.

### 2.2. 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 ( $2 \text{ g L}^{-1}$ , i.e. initial total organic carbon (TOC),  $1120 \text{ mg L}^{-1}$ ) and 0.5 g catalyst. After the reactor was outgassed with argon, the mixture was heated to the reaction temperature under stirring over a period of ca. 0.5 h. Then, the stirrer was stopped and the air was admitted into the reactor until the predefined pressure was reached. The reaction finally started when the stirring was switched on. This point was taken as “zero time” and one sample was withdrawn to measure the

exact initial concentration of 2-CP. The 2-CP adsorption and/or dechlorination could be evaluated by comparison to the concentration of 2-CP introduced. Other 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 HPLC (Shimadzu) with a  $250 \text{ mm} \times 4.6 \text{ mm}$  C18 reverse phase column (UP 5MM1-25QS, Interchim). The mobile phase was a mixture of 20 vol.% methanol and 80 vol.% water (flow rate,  $1 \text{ mL min}^{-1}$ ). The HPLC system was equipped with a UV-vis detector set at 210 and 281 nm.

TOC in the liquid sample was measured with a Shimadzu 5050 TOC analyzer after subtraction of the inorganic carbon (IC) contribution to the total carbon (TC).

The pH of the liquid samples was measured using a pH meter (Radiometer Analytical PHM240).

## 3. Results and discussion

Mass transfers in liquid phase reactions are directly influenced by the efficiency of the stirring setup. Therefore, as a preliminary work, we investigated the effect of the rotation speed. Table 1 shows the initial rates for 2-CP abatement over 3 wt.%  $\text{Ru/ZrO}_2$  catalyst, ex  $\text{RuCl}_3$ , at different rotation speeds. These results indicate that 1000 rpm is enough to ensure a vigorous and homogenous mixing of the reaction mixture with our experimental setup. Obviously, such an optimum cannot be translated directly to a different reactor and very different stirring conditions, as low as 150 rpm, are reported in the literature [20]. In the following, to make sure that the effect of the rotation speed can be excluded, that is no mass transfer limitation in the liquid phase, the rotation speed was set at 1300 rpm.

### 3.1. Catalytic and non-catalytic wet air oxidation of 2-CP

Fig. 1 shows the evolution as a function of time of the 2-CP conversion, the TOC removal value and the pH upon catalytic and non-catalytic WAO of a  $2 \text{ g L}^{-1}$  2-CP aqueous solution at 413 K. In the absence of catalyst, the WAO of 2-CP is very slow. Even after 24 h, 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 [20,26]. 2-CP is a relatively thermally stable molecule under the applied reaction conditions.

After introducing the  $\text{Ru/ZrO}_2$  catalyst, ex  $\text{RuCl}_3$ , the reaction was significantly accelerated. In fact, over this catalyst,

Table 1  
Initial rates of 2-CP abatement at different rotation speeds

Rotation speed (rpm)	Initial rate of 2-CP ( $\text{mol}_{2\text{-CP}} \text{ mol}_{\text{Ru}}^{-1} \text{ h}^{-1}$ )
700	6.8
1000	8.7
1300	8.5
1500	8.9

0.5 g 3 wt.%  $\text{Ru/ZrO}_2$  ( $\text{RuCl}_3$ ) catalyst, 413 K, 5 MPa, 1300 rpm and  $[\text{2-CP}]_0 = 2 \text{ g L}^{-1}$ .

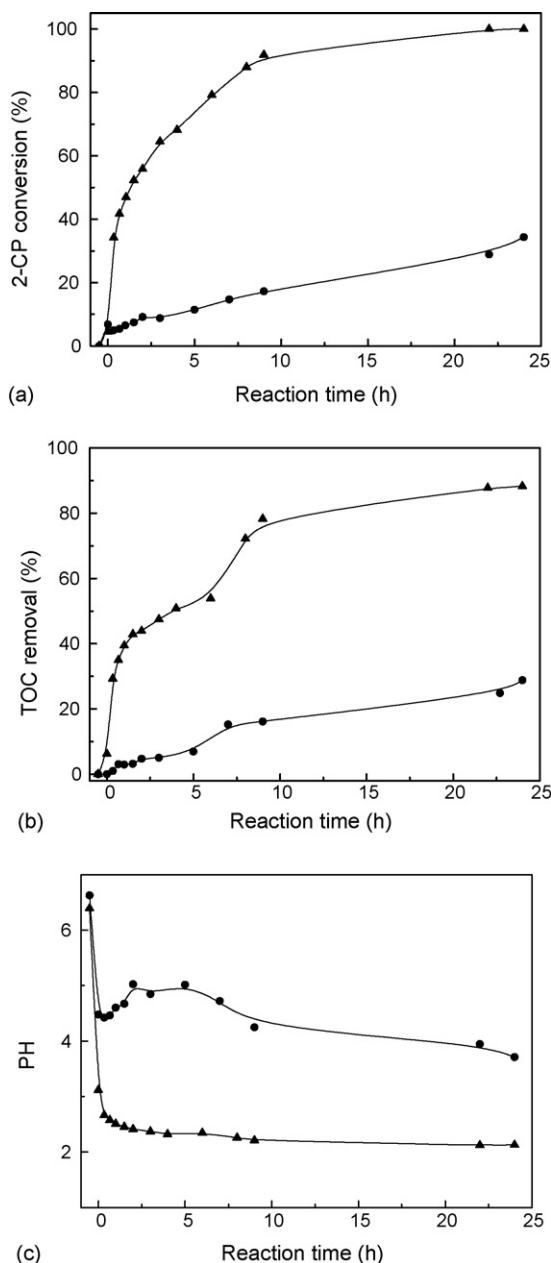


Fig. 1. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the wet air oxidation (WAO) of 2-CP without catalyst (●) or over 3 wt.% Ru/ZrO<sub>2</sub> (RuCl<sub>3</sub>) (▲) [0 or 0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

2-CP was completely converted after 24 h and TOC abatement reached 88% by that time. From these results, one can conclude that Ru/ZrO<sub>2</sub> is an effective catalyst for the CWAO of 2-CP.

Furthermore, one can notice that the 2-CP conversion at zero time is not 0. The partial dechlorination or the adsorption of 2-CP to the catalyst surface might be responsible for that. This hypothesis was further confirmed by looking at the TOC results. In fact, the TOC abatement at zero time is about 0 in the absence of any catalyst, while, it is 6% over Ru/ZrO<sub>2</sub>, which value is almost the same as the observed 2-CP conversion (4%). Therefore, we think the TOC removal at zero time (TOC<sub>0</sub>) can be used to quantify the initial adsorption of 2-CP on the catalyst surface.

The initial pH of the 2-CP solution was about 6.3. Upon the WAO reaction, the pH of the solution decreases (Fig. 1). This decrease is more obvious in the presence of the catalyst. Such an increase of the acidity is directly related to the degradation of 2-CP and the formation of small organic acids as well as HCl (2-CP dechlorination) [20]. In fact, a deeper oxidation is observed in the presence of Ru/ZrO<sub>2</sub>. As a result, smaller (and stronger) acids are generated and a lower pH is measured at the end of the reaction. From the analysis, small chain carboxylic acids such as acetic acid, chloroacetic acid and succinic acid could be identified. Consequently, although a significant degassing of the CO<sub>2</sub> dissolved in water at high pressure occurs upon sampling, a rapid measure of the final pH might already give some qualitative information about the degradation degree of the 2-CP molecule.

As reported in the literature [16,20], we also confirmed the existence in the liquid samples of trace amounts of aromatic intermediates, such as catechol, chlorohydroquinone, hydroquinone, chloro-*p*-benzoquinone and benzoquinone.

Finally, after calculating the selectivity of the reaction by dividing the TOC removal by the 2-CP conversion, we found that the selectivity is higher than 74% all along the 24 h reaction, indicating that Ru/ZrO<sub>2</sub> is so efficient that most of the 2-CP was directly mineralized to CO<sub>2</sub>, H<sub>2</sub>O and HCl. In fact, after 24 h, 2-CP is nearly completely mineralized (88%) under such conditions.

### 3.2. Effect of experimental parameters on the catalytic performances of Ru/ZrO<sub>2</sub>

#### 3.2.1. Ru precursor

We investigated the effect of the nature of the Ru precursor (RuCl<sub>3</sub> versus Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) on the catalytic performances of 3 wt.% Ru/ZrO<sub>2</sub> catalysts. The results are presented in Fig. 2. As demonstrated earlier by Besson et al. in the CWAO of *p*-hydroxybenzoic acid [27], we observed that the catalyst prepared from Ru(NO)(NO<sub>3</sub>)<sub>3</sub> as the Ru precursor, was slightly more active, even though higher initial rates could be measured when RuCl<sub>3</sub> was used as a precursor (which is the reason why we measured the mass transfer limitation over the Ru/ZrO<sub>2</sub> ex RuCl<sub>3</sub>). In fact, over the 3 wt.% Ru/ZrO<sub>2</sub> catalyst prepared with Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, almost complete 2-CP conversion and higher TOC removal could be obtained at shorter time of reaction. Therefore, we think Ru(NO)(NO<sub>3</sub>)<sub>3</sub> is better than RuCl<sub>3</sub> to act as a Ru precursor for the preparation of Ru/ZrO<sub>2</sub> catalysts. Besson et al. [27] have already characterized the Ru dispersion of identical Ru/ZrO<sub>2</sub> catalysts prepared from different metal precursor. According to their report, the average Ru particle size in the catalysts prepared from RuCl<sub>3</sub> and Ru(NO)(NO<sub>3</sub>)<sub>3</sub> were respectively 2.9 and 2.5 nm. Apart the metal distribution at the oxide surface (accessibility) that might be different depending on the metal precursor which is used [27], one could also imagine that the presence of some residual chlorine at the catalyst surface may hinder the reaction. In fact, when chlorinated metal precursors are used for the preparation, some chlorine sits at the metal-support interface [28,29]. It has been demonstrated earlier that such chlorine species would

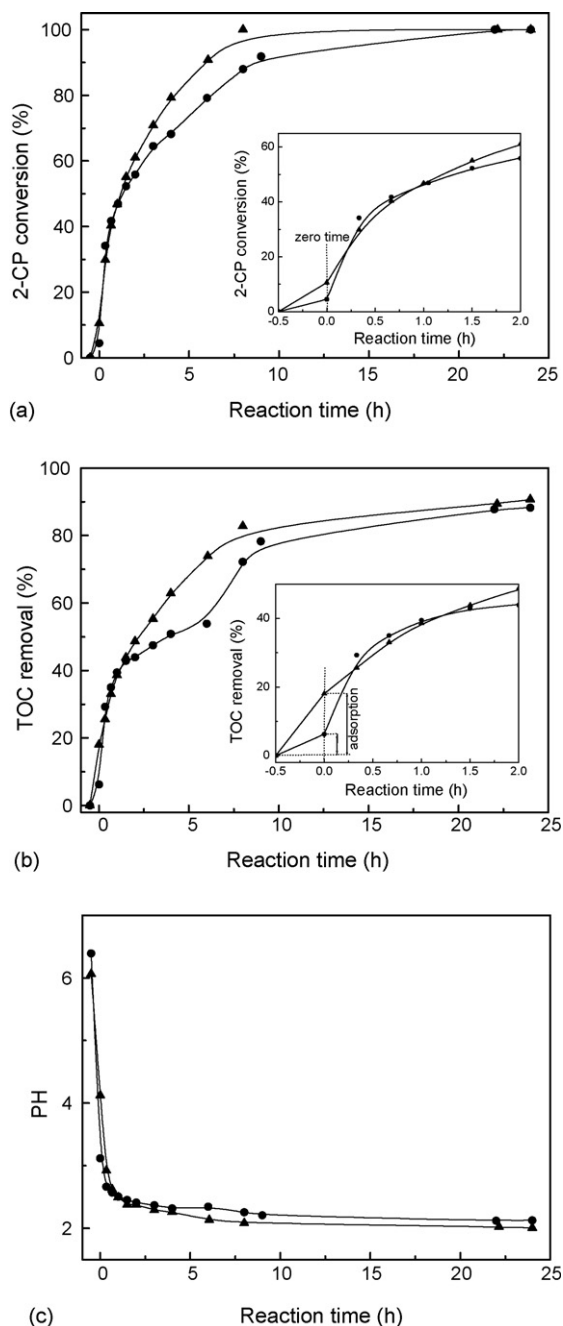


Fig. 2. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the catalytic wet air oxidation (CWAO) of 2-CP over 3 wt.%  $\text{Ru}/\text{ZrO}_2$  prepared from  $\text{RuCl}_3$  (●) or from  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (▲) as the ruthenium precursor [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm,  $[\text{2-CP}]_0 = 2 \text{ g L}^{-1}$ ].

prevent the oxygen diffusion from the oxide to the metal particle and vice-versa [30]. Consequently, if the oxygen mobility at the catalyst surface is somehow blocked when chlorinated precursors are used, the reactivity of such catalysts would directly be negatively impacted. There is also another possibility, that is, a Cl migration towards specific sites where they have a more severe poisoning effect. Furthermore, it can be noticed from Fig. 2b that the TOC removal at zero time over 3 wt.%  $\text{Ru}/\text{ZrO}_2$  ex  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  (18%) is much higher than that over 3 wt.%  $\text{Ru}/\text{ZrO}_2$  ex  $\text{RuCl}_3$  (6%). On the bare support,

the TOC removal at zero time was 15%. Such an observation would also suggest that 2-CP adsorption is somehow hindered in the presence of chlorine on the catalyst surface. In the following work,  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  only is used for the catalyst preparation.

Finally, one might note that when  $\text{RuCl}_3$  was used, the initial pH ( $t = 0$ ) of the solution (3.1) is lower than the one measured when  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  is used (4.1). This result might be explained by the presence of some residual  $\text{Cl}^-$  on the catalyst surface which might dissolve into the solution as hydrochloric acid (hydrolysis reaction). Later, as the reaction proceeds, more acids (essentially more  $\text{HCl}$ ) would be generated over the 3 wt.%  $\text{Ru}/\text{ZrO}_2$  catalyst prepared with  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  which is more active and pH would reach the same value as for the catalyst prepared with  $\text{RuCl}_3$ . Of course, another explanation would be that zero time is not rigorously the same for the two experiments. At the very beginning of the reaction the pH decreases sharply in a very short period of time. Any difference for  $t = 0$  might explain this initial difference in pH. The first sample ( $t = 0$ ) might have been withdrawn a fraction of a minute later in the case of  $\text{Ru}/\text{ZrO}_2$  ex  $\text{RuCl}_3$  and the reaction might have already proceeded. Furthermore, as stated above, when chlorinated metal precursors are used for the preparation of supported metal catalysts, chlorine essentially sits at the metal-support interface, even after reduction of the catalyst under hydrogen [28,29]. Such strongly adsorbed chlorine species would probably hardly dissolve into the solution to form  $\text{HCl}$  upon reaction and the second explanation might be preferred.

### 3.2.2. Reaction temperature

The influence of the reaction temperature was studied in the range 403–433 K. Fig. 3 shows the evolution of the 2-CP conversion, the TOC removal and the pH upon reaction over a 3 wt.%  $\text{Ru}/\text{ZrO}_2$  ex  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  catalyst at different temperatures. Just as we anticipated, the 2-CP conversion and the TOC removal increased with temperature. As a result, the pH of the solution also decreased faster when increasing the temperature. As a conclusion, higher temperatures are favorable for the CWAO of 2-CP. However, higher temperatures practically translate into higher operating costs and severe corrosion problems due to the presence of  $\text{HCl}$  generated during the reaction. 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. In order to observe the effects of other operating parameters, the reaction should not be too fast either. Taking into consideration the above-mentioned multisided reasons, we considered 413 K as the optimum temperature for the study of the CWAO of 2-CP over  $\text{Ru}/\text{ZrO}_2$  catalysts. Fig. 3b shows that TOC removal values at zero time and different temperatures are almost the same ( $\sim 18\%$ ). 2-CP is strongly adsorbed on the catalyst surface, and the reaction temperature has no effect on the initial adsorption of 2-CP within the investigated temperature range.

Finally, from the Arrhenius plot ( $\ln r_{0(2\text{-CP})}$  versus  $1/T$ ) for the evolution of the initial rate of 2-CP removal as a function of temperature, the apparent activation energy for the CWAO of

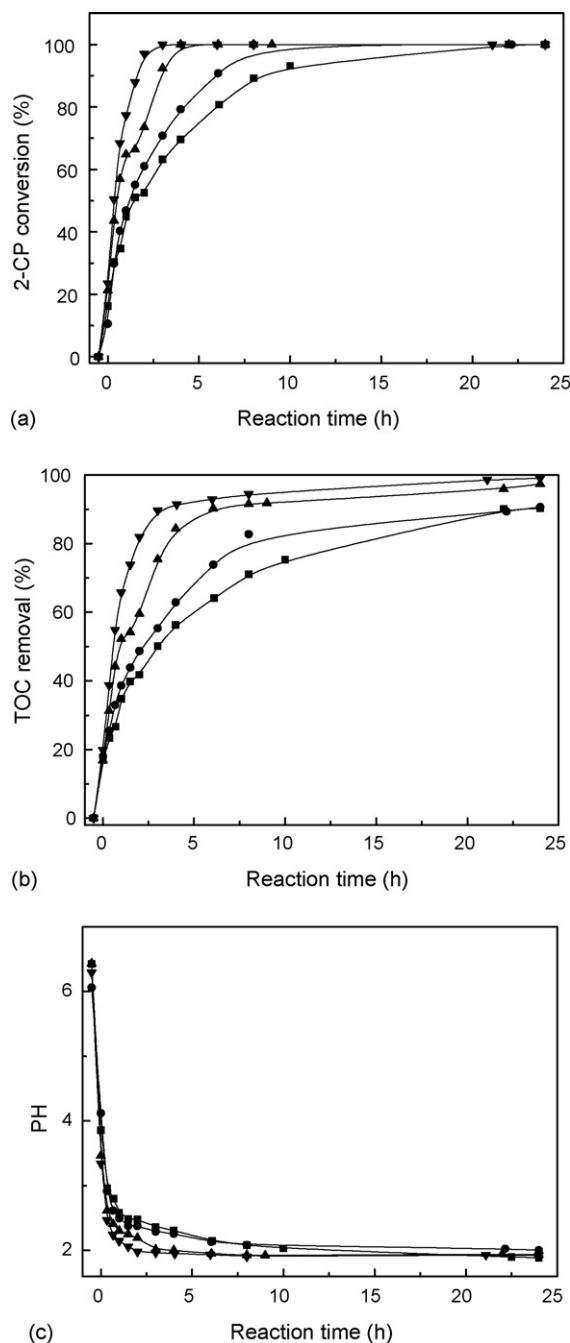


Fig. 3. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the CWAO of 2-CP over 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) at 403 K (■), 413 K (●), 423 K (▲) and 433 K (▼) [0.5 g catalyst, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

2-CP was calculated to be 36 kJ mol<sup>-1</sup> ( $r$  parameter:  $-0.9981$ ). Joglekar et al. [26] reported that the activation energy for the WAO of 2-CP is 138 kJ mol<sup>-1</sup> during the induction period and 145 kJ mol<sup>-1</sup> upon steady state operation. So, in the presence of the Ru/ZrO<sub>2</sub> catalyst, the activation energy for the elimination of 2-CP is clearly decreased and the reason for the promoting effect of Ru/ZrO<sub>2</sub> is clearly identified. It was previously reported that the activation energy is 34 kJ mol<sup>-1</sup> for the CWAO of phenol over Pt-Ru/C [31]. Such values are strictly comparable. Not surprisingly, activation energies for the

elimination of the smaller organic acids, which are refractory to the oxidation, are higher. It was calculated that the activation energy is 125 kJ mol<sup>-1</sup> for the CWAO of succinic acid over Ru/TiO<sub>2</sub> [32] and 101 kJ mol<sup>-1</sup> for the CWAO of acetic acid over Ru/C [33].

### 3.2.3. Total pressure

It has been found earlier that the partial pressure of O<sub>2</sub> has some impact on both the conversion and the mineralization of phenol and succinic acid upon CWAO [32,34,35]. This effect might be related to the availability of oxygen to the active site. The partial pressure of oxygen in the gas phase will partly determine the concentration in oxygen in the liquid phase. According to the Henry's law, the concentration of O<sub>2</sub> dissolved in the liquid phase is proportional to the partial pressure of O<sub>2</sub> in the gas phase. Furthermore, let us note that the total pressure in the gas phase results from the sum of the initial Ar atmosphere after the reactor has been purged at room temperature, the autogenous pressure which appears upon heating (essentially water vapor), and the air pressure balance. Taking into account that, at 413 K, the saturated water vapor pressure is 0.36 MPa and that the argon pressure was 0.14 MPa, when the total pressure is 5 MPa, the partial pressure of air and oxygen are 4.5 and 0.9 MPa, respectively, the oxygen solubility is ca. 0.26 g L<sup>-1</sup> [17].

Additionally, it was calculated from reaction (1) that the stoichiometric amount of oxygen, required for the complete oxidation of 2-CP to CO<sub>2</sub> and H<sub>2</sub>O under our reaction conditions, corresponds to 0.27 MPa, that is the air pressure should be higher than 1.35 MPa:



Consequently, the minimum total pressure was set at 2 MPa to avoid any parallel reactions, such as the polymerization.

We investigated the effect of the total pressure (between 2 and 6 MPa) using 3 wt.% Ru/ZrO<sub>2</sub>, ex Ru(NO)(NO<sub>3</sub>)<sub>3</sub> at 413 K. As shown in Fig. 4a, the conversion of 2-CP improved when the total pressure increased. This effect was only noticeable when the total pressure increased from 2 to 4 MPa, while the difference between 4 and 6 MPa was somewhat insignificant. The oxygen diffusion to the catalyst surface is not limiting anymore for the reaction and, above 4 MPa, the CWAO of 2-CP transforms from oxygen diffusion-controlled to kinetic-controlled. This behavior is clearly exemplified in Fig. 5 (initial rate for 2-CP abatement versus total pressure and oxygen partial pressure). When total pressure is below 4 MPa, the initial rate for the 2-CP elimination is first order with respect to the oxygen pressure. Above this limit, the conversion of 2-CP is zero order with respect to the oxygen pressure. These results are similar to what has been found by Joglekar et al. [26] in the WAO of phenol and 2-CP (in the absence of any catalyst) and Chang et al. [35] in the CWAO of phenol over CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. When we increased the total pressure from 2 to 6 MPa, the TOC removal values at zero time and different oxygen partial pressure were almost the same (14–18%). This result suggests that the partial pressure of oxygen has no effect on the adsorption of 2-CP on the catalyst surface.

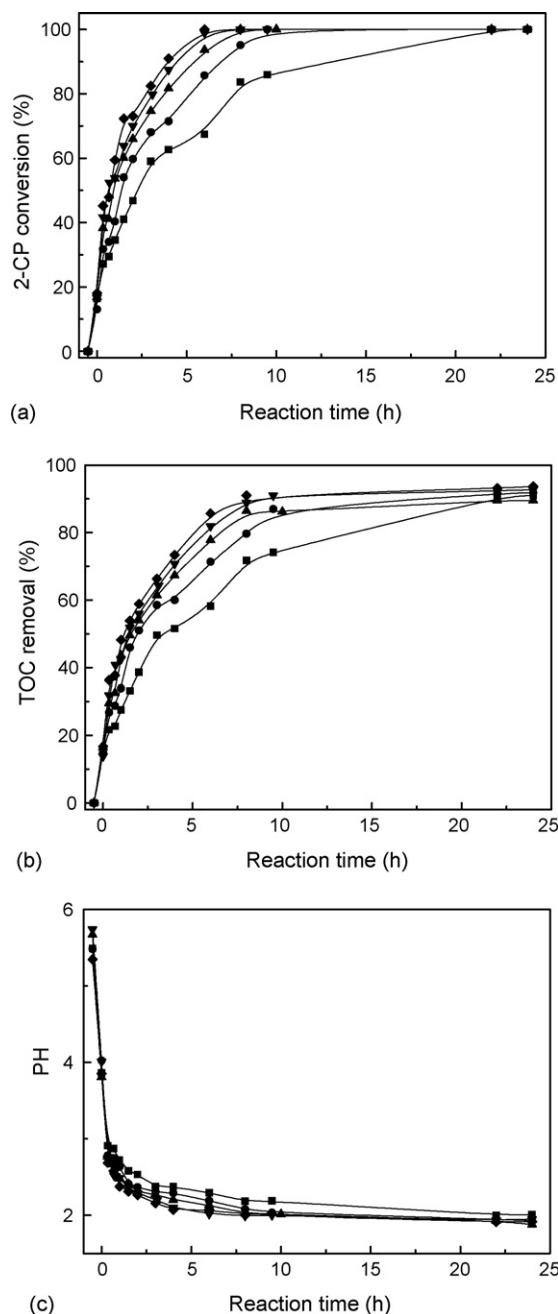


Fig. 4. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the CWAO of 2-CP over 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) at 2 MPa (■), 3 MPa (●), 4 MPa (▼), 5 MPa (▲) and 6 MPa (◆) [0.5 g catalyst, 413 K, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

The total pressure had a greater effect on the TOC removal than on the 2-CP conversion at least at short contact time. Within the investigated pressure range (2–6 MPa), the TOC abatement increased continuously with the total pressure (Fig. 4b). These results are analogous with what has been found in the CWAO of phenol [34,35] and can be explained by the fact that the total mineralization of 2-CP needs more oxygen.

### 3.2.4. Initial 2-CP concentration

Fig. 6 shows the result for the CWAO of 2-CP solutions (0.2–2 g L<sup>-1</sup>) over 3 wt.% Ru/ZrO<sub>2</sub>, ex Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, at 413 K

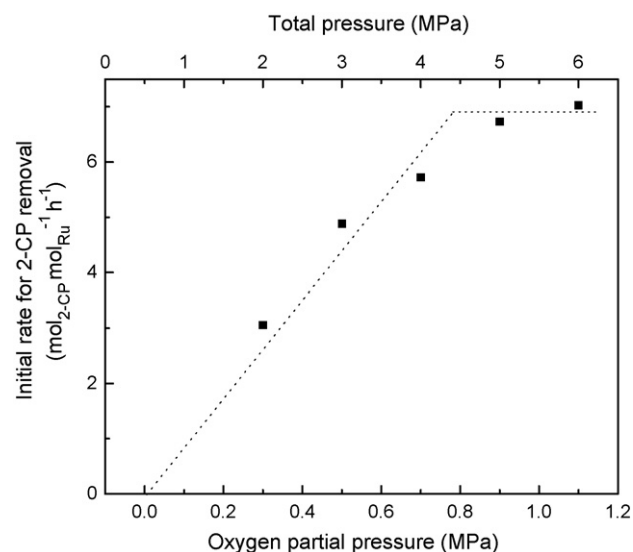


Fig. 5. Evolution of the initial rate of 2-CP conversion as a function of the total pressure [0.5 g 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>), 413 K,  $P$ : 2–6 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>].

and 5 MPa total pressure. The initial rate for the 2-CP elimination is about constant (Table 2). There is only one singular point, when the concentration of 2-CP is as low as 0.2 g L<sup>-1</sup>. In this case, a much lower initial rate of 2-CP abatement was measured. However, with such a low amount of 2-CP in the solution, the fraction of the 2-CP molecules which are initially adsorbed on the catalyst surface might become predominant and the initial rate of reaction cannot be accurately determined. Furthermore, as far as HPLC is used for the liquid phase analysis, some inaccuracies in the concentration determination might have a strong impact. These results suggest that the reaction order is zero with respect to the initial 2-CP concentration and can be explained by the saturation of the active sites on the Ru/ZrO<sub>2</sub> surface with 2-CP molecules.

From Fig. 7, it can be seen that the initial 2-CP adsorption over Ru/ZrO<sub>2</sub> is almost proportional to the initial 2-CP concentration and then levels off when the initial 2-CP concentration is higher than 1 g L<sup>-1</sup>. The maximum 2-CP adsorption capacity for the catalyst is about 60 mg<sub>2-CP</sub> g<sub>catalyst</sub><sup>-1</sup> and a Langmuir–Hinshelwood type of adsorption isotherm is observed.

Furthermore, it is worthy noticing that the evolution of pH as a function of time (Fig. 6c) is also peculiar when the initial 2-CP

Table 2

Initial rates of 2-CP abatement of 2-CP solutions with different initial concentrations

Concentration of 2-CP solution (g L <sup>-1</sup> )	Initial rate of 2-CP abatement (mol <sub>2-CP</sub> mol <sub>Ru</sub> <sup>-1</sup> h <sup>-1</sup> )
0.2	2.8
0.5	6.4
1	6.3
2	6.7

0.5 g 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) catalyst, 413 K, 5 MPa and 1300 rpm.

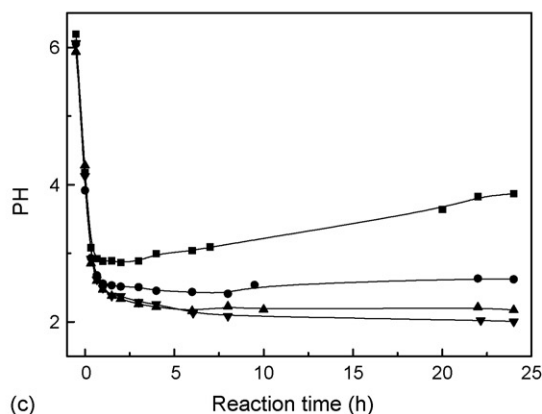
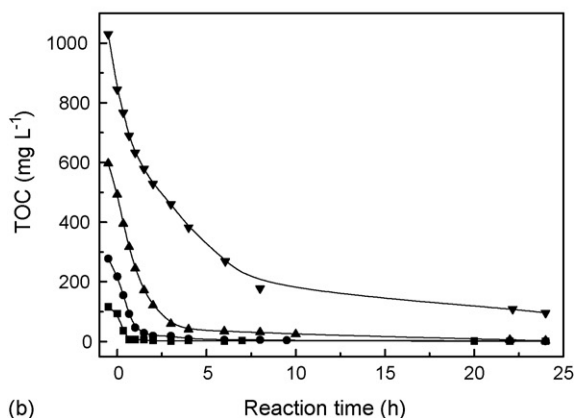
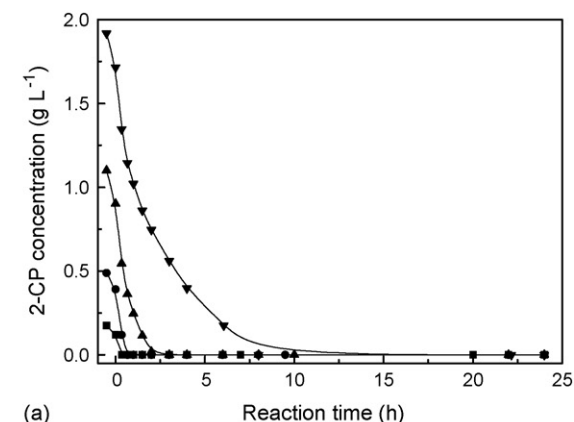


Fig. 6. Evolution of the 2-CP concentration (a), the TOC (b) and the pH (c) in the CWAO of 2-CP over 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 0.2 g L<sup>-1</sup> (■), 0.5 g L<sup>-1</sup> (●), 1 g L<sup>-1</sup> (▲), 2 g L<sup>-1</sup> (▼)].

concentration is 0.2 g L<sup>-1</sup>. Because the initial 2-CP concentration is very low, less HCl is generated after the total mineralization of 2-CP and the minimum pH is higher. Furthermore, at the end of the reaction, the pH of the solution increased. This result is consistent with the higher TOC removal observed in this case and can be explained by the total mineralization of the 2-CP molecules to CO<sub>2</sub> and H<sub>2</sub>O. These two phenomena explain the different trends observed in the pH evolution.

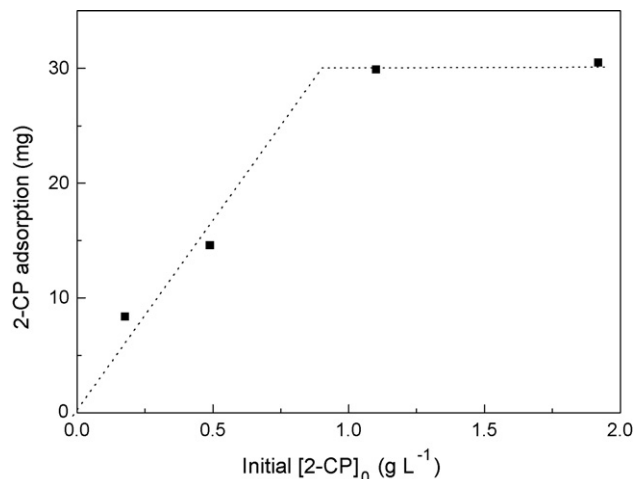


Fig. 7. Evolution of the 2-CP adsorption as a function of the initial 2-CP concentration [0.5 g 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>), 413 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 0.2–2 g L<sup>-1</sup>].

### 3.2.5. Initial pH value of the 2-CP solution

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 and 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/ZrO<sub>2</sub>, ex Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, at 413 K and under 5 MPa total pressure. Either H<sub>3</sub>PO<sub>4</sub> or NaOH were used to adjust the initial pH to the desired value.

Fig. 8 shows the results. It is clear that both the 2-CP conversion and the TOC removal increased when increasing the initial pH from 2 to 10. Then, increasing the pH from 10 to 12, the initial 2-CP conversion rate went on increasing but the TOC abatement stayed almost constant. These results are similar to what has been found by Kojima et al. on Ru/TiO<sub>2</sub> [20] and can be explained by the conflict that somehow exists between the dechlorination reaction of the 2-CP molecule and the surface adsorption properties of the Ru/ZrO<sub>2</sub> catalyst. On one hand, as found by Kojima et al. [20] in the WAO of 2-CP, higher initial pH can prompt the conversion of 2-CP because the dechlorination reaction is accelerated. This may be the reason why 2-CP conversion and TOC removal increased when the initial pH increased from 2 to 10. On the other hand, too high pH will lead to the negative charging of the zirconia surface. Such phenomenon may hinder the adsorption of some negatively charged chemical species because of the electrostatic barrier and therefore limit the subsequent total oxidation of the intermediates. To check this, we measured the pH at the point of zero charge (pH<sub>PZC</sub>) for the ZrO<sub>2</sub> support using the method already described by Brunelle [36]. The pH<sub>PZC</sub> for the ZrO<sub>2</sub> support we used in this study was measured as 6.1. The pK<sub>a</sub> of 2-CP, acetic acid, chloroacetic acid and succinic acid are 8.5, 4.8, 2.9 and 4.2, respectively. From Fig. 8c, one can see that the pH of the solution, when the initial pH is 12.1, is about higher than 6.1 all along the reaction. This situation is different from what is



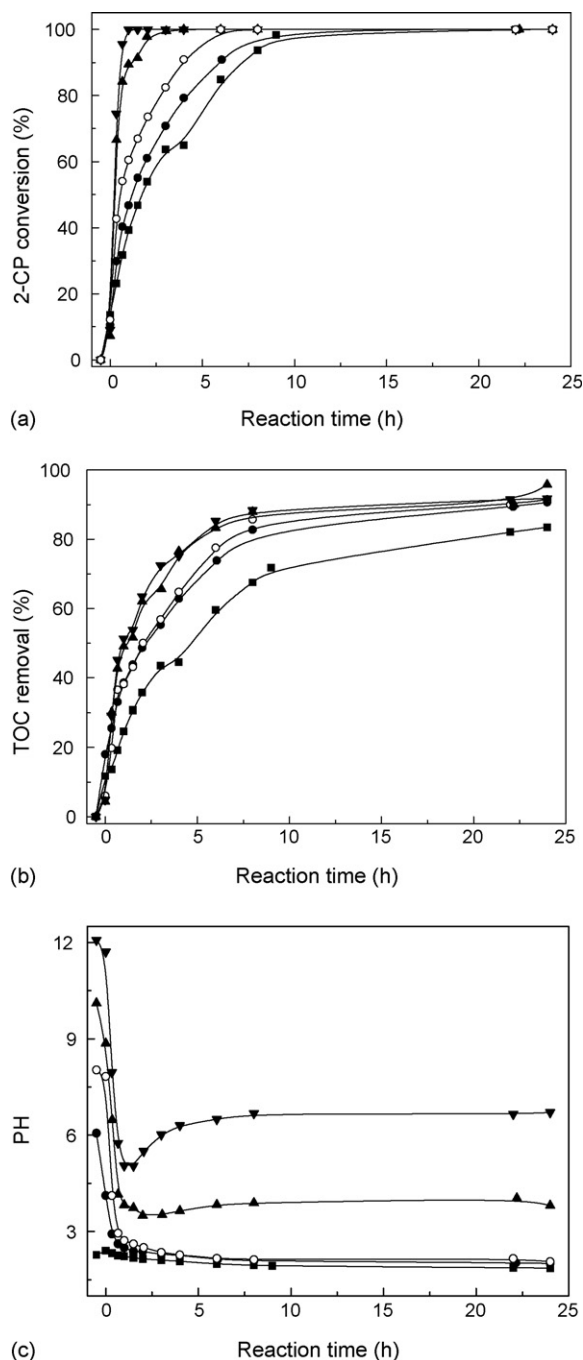


Fig. 8. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the CWAO of 2-CP over 3 wt.% Ru/ZrO<sub>2</sub> (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [2-CP]<sub>0</sub> = 2 g L<sup>-1</sup>, initial pH 2.3 (■), 6.1 (●), 8.0 (○), 10.1 (▲), 12.1 (▼)].

observed at lower initial pH. Consequently, the surface of ZrO<sub>2</sub> is almost constantly negatively charged. Furthermore, most of the organic acids exist in the form of anions at such pH. Then, it is difficult for the acids to adsorb on the catalyst surface and the TOC abatement is limited. This is the reason why there are different trends between the 2-CP conversion and the TOC removal after increasing of initial pH of the 2-CP solution from 10 to 12. Consequently, pH 10 might be considered as the optimum.

The TOC removal values at zero time when initial pH 2.3, 6.1, 8.0, 10.1, and 12.1 were 12, 18, 6, 4, and 5%, respectively. From these results, we can see that the adsorption of 2-CP increased with pH at the beginning, reached a maximum when initial pH is 6.1, then decreased with increasing pH. This is comprehensible because when the initial pH is 6.1, the surface of the catalyst (pH<sub>PZC</sub> 6.1) is neutral, and there is no electrostatic barrier to prevent the adsorption of the reaction intermediates.

Finally, one can notice that, when the initial pH is greater than 10, the pH of the solution first decreases and then increases at the end of the reaction. This result is similar to what we observed at very low 2-CP initial concentration and can be explained by the deeper oxidation of the organic acids to CO<sub>2</sub> and H<sub>2</sub>O. This trend for the evolution of the pH as a function of time is even more pronounced when the initial pH is 12.1. However, when the initial pH of the solution is 10.1 and 12.1, the minimum pH upon reaction is 3.5 and 5, respectively, and the final pH of the solution is about 4.0 and 6.7, respectively. Such differences might derive from different reaction routes and explain the differences in the catalyst performances (2-CP conversion, TOC abatement, etc.).

### 3.2.6. Leaching of Ru

The Ru concentration in the liquid phase after 24 h reaction was repeatedly measured by ICP-AES. As earlier reported in the CWAO on the Ru/ZrO<sub>2</sub> catalyst [22,25], no Ru could be detected. The Ru concentration in the solution was systematically lower than 0.5 ppm which is the detection limit of the ICP-AES equipment we used.

## 4. Conclusions

It was demonstrated that Ru/ZrO<sub>2</sub> is an efficient catalyst for the CWAO of 2-CP. Over this type of catalyst and high 2-CP conversion and TOC removal can be reached at mild reaction temperature (413 K) and moderate pressure (5 MPa). The efficiency of Ru/ZrO<sub>2</sub> is very high, only little amount of intermediates were observed during the reaction. Ru(NO)(NO<sub>3</sub>)<sub>3</sub> appeared as the optimum precursor for the preparation of Ru/ZrO<sub>2</sub> catalysts, because 2-CP adsorption is favored in the absence of any chlorine on the catalyst surface. The activation energy for this reaction was calculated to be 36 kJ mol<sup>-1</sup>. The CWAO of 2-CP is first order in oxygen when the total pressure is lower than 4 MPa. Above 4 MPa, the reaction shifts from oxygen diffusion controlled to kinetic controlled, and the CWAO of 2-CP changes from first order to zero order with respect to the oxygen partial pressure. Additionally, the 2-CP removal rate is zero order with respect to the initial 2-CP concentration due to the saturation of the Ru/ZrO<sub>2</sub> surface with 2-CP molecules. Alkaline conditions favor the conversion of 2-CP by accelerating the dechlorination reaction. However, too high pH also hinder the total mineralization of 2-CP by preventing the adsorption of the intermediates on the catalyst surface (electrostatic barrier). Initial pH 10 should be preferred.

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