Catalytic wet air oxidation of chlorophenols over supported ruthenium catalysts

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Abstract

A series of noble metal (Pt, Pd, Ru) loaded zirconia catalysts were evaluated in the catalytic wet air oxidation (CWAO) of mono-chlorophenols (2-CP, 3-CP, 4-CP) under relatively mild reaction conditions. Among the investigated noble metals, Ru appeared to be the best to promote the CWAO of CPs as far as incipient-wetness impregnation was used to prepare all the catalysts. The position of the chlorine substitution on the aromatic ring was also shown to have a significant effect on the CP reactivity in the CWAO over 3 wt.% Ru/ZrO_2. 2-CP was relatively easier to degradate compared to 3-CP and 4-CP. One reason could be the higher adsorption of 2-CP on the catalyst surface. Further investigations suggested that 3 wt.% Ru/ZrO_2 is a very efficient catalyst in the CWAO of 2-CP as far as high 2-CP conversion and TOC abatement could still be reached at even lower temperature (393 K) and lower total pressure (3 MPa). Additionally, the conversion of 2-CP was demonstrated to increase with the initial pH of the 2-CP solution. The dechlorination reaction is promoted at higher pH. In all cases, the adsorption of the reactants and the reaction intermediates was shown to play a major role. All parameters that would control the molecule speciation in solution or the catalyst surface properties would have a key effect.

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1. Introduction

More and more attention is being paid to the environment and the preservation of the water resources and quality is among the priority objectives. As a result, the removal of the toxic organic compounds from aqueous wastewaters has attracted a lot of research [1–5]. Among the different pollutants encountered in the industrial wastewaters, the chlorophenols (CPs) are very important chemical compounds and intermediates in several chemical industries. Such compounds are toxic, hardly biodegradable, difficult to remove from the environment and 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]. Consequently, to protect the environment, it is necessary to develop some highly efficient techniques for the treatment of such organic-contaminated wastewater. Among the various 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 to CO_2, H_2O and HCl, using oxygen as the oxidant.

Generally, the WAO of organic compounds without catalyst was performed under high pressure (5–17.5 MPa) and 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 generated 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 $CuSO_4$, MnO_2 and Co_2O_3 in the CWAO of 4-CP in the temperature range 423–473 K. Qin et al. [18] investigated the activities of Pt,

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Pd and Ru loaded alumina, ceria and activated carbon catalysts in the CWAO of 4-CP at 453 K. Posada et al. [19] also studied the CWAO of 2-CP over Cu loaded ceria catalysts at 433 K. However, the operating temperature for these catalysts was relatively high. Recently, Kojima et al. [20] found that Ru loaded TiO$_2$ catalyst was active for the CWAO 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 CWAO of 2-CP in a trickle bed reactor and obtained about 55% 2-CP conversion and 50% TOC removal at the same temperature (413 K). However, continuous efforts are still necessary to optimize the experimental conditions and to find some new highly efficient catalysts operating at lower temperature. In previous works of our group, Ru loaded zirconia (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], *p*-coumaric acid [25] and *o*-chlorophenol [26]. In this work, we studied the catalytic performances of a series of noble metal (Pt, Pd, Ru) loaded ZrO$_2$ catalysts for the CWAO of 2-CP. Then, the emphasis was put on Ru/ZrO$_2$. The effects of the chlorine position, the operating temperature and/or pressure and the initial pH of 2-CP solution were also investigated.

2. Experimental

2.1. Catalyst preparation

Noble metal (Pt, Pd, Ru) loaded zirconia catalysts were prepared as described previously [25]. The ZrO$_2$ support was supplied by Melcat (XZ0 923/01, particle size = 15–20 μm). Pt, Pd or Ru were introduced by incipient-wetness impregnation using aqueous solutions of Pt(NH$_3$)$_4$(NO$_3$)$_2$ (Aldrich), Pd(NH$_3$)$_4$(NO$_3$)$_2$ (Aldrich) or Ru(NO)(NO$_3$)$_3$ (Alfa Aesar). The Pt, Pd and Ru concentrations in the starting aqueous solutions were accurately determined by ICP-AES. After impregnation, the preparation was dried for 24 h at room temperature, introduced in a quartz tube reactor, reduced in flowing hydrogen (15 L h^{-1}) at 573 K for 2 h (temperature ramp rate: 1 K min^{-1}). After cooling down to room temperature under H$_2$, the cell was purged with argon and the catalyst was further passivated at room temperature under flowing 1% O$_2$/N$_2$ (15 L h^{-1}) for 2 h.

2.2. Characterization

2.2.1. XRD
XRD patterns were obtained on a Siemens D5005 diffractometer (Cu Kα, 0.15406 nm). The average crystallite size was estimated using the Debye-Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the average crystallite size (nm), λ the wavelength (nm), β the corrected full width at half maximum (radian) and θ is the Bragg angle (radian).

Rietveld refinement calculations, which are based on the fitting of the entire diffraction pattern using the least-square method, were also performed, especially to determine the metal crystallite size as far as the diffraction lines for the metal and the zirconia support overlapped.

2.2.2. Specific surface area
The specific surface area of the catalysts was 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.

2.3. 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 CP aqueous solution (2 g L^{-1}, i.e. initial total organic carbon (TOC): 1120 mg L^{-1}) and 0.5 g catalyst. After the reactor was outgassed with argon, the mixture was heated to the desired 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 stirrer was switched on. This point was taken as "zero time" and one sample was withdrawn to measure the exact initial concentration of CP and deduce the fraction of CP which is initially adsorbed at the catalyst surface and/or already reacted (thermal decomposition, dechlorination, ...). Further liquid samples were periodically withdrawn from the reactor, centrifugated to remove any catalyst particle in the liquid sample, and finally analyzed.

The substrates and the reaction intermediates were analyzed via HPLC (Shimadzu) using a 250 mm × 4.6 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 mL min^{-1}). The HPLC system was equipped with a UV–vis detector set at 210 and 281 nm.

The total organic carbon 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). Furthermore, the carbon mass balance in the liquid phase could be checked by comparing the TOC values with the total carbon concentrations in the liquid derived from HPLC analysis (residual CP + identified/quantified reaction intermediates).

The pH of the liquid samples was measured immediately after taken from the reactor using a pH meter (Radiometer analytical PHM240).

The metal concentration in the liquid phase after 24 h reaction was also repeatedly measured by ICP-AES. As earlier reported in the CWAO over Ru/ZrO$_2$ catalysts [22,25], no metal could ever be detected. The metal concentration in the solution was systematically lower than 0.5 ppm (detection limit), indicating that leaching does not occur.
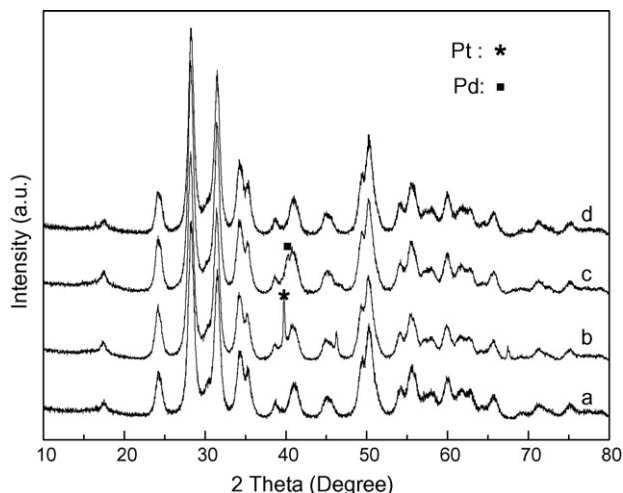
Fig. 1. XRD patterns of the ZrO_2 (a), 3 wt.% Pt/ZrO_2 (b), 3 wt.% Pd/ZrO_2 (c) and 3 wt.% Ru/ZrO_2 (d).

3. Results and discussion

3.1. Characterization

3.1.1. XRD

Fig. 1 shows the XRD patterns of the bare ZrO_2 support and the different catalysts. The ZrO_2 support consists of a mixture of two phases: monoclinic and tetragonal. The average ZrO_2 crystallite size was estimated to be 9.3 nm. No change was noticeable in the ZrO_2 structure and/or the average ZrO_2 crystallite size upon impregnation and reduction under H_2 at 300 °C.

In the case of 3 wt.% Ru/ZrO_2, the XRD pattern was identical to the one of the pure ZrO_2 support. No diffraction peak characteristic of the ruthenium phase could be observed, indicating that the Ru particles are probably well-dispersed on the zirconia support.

On the contrary, a diffraction peak at about 40°, characteristic for Pt(1 1 1) and Pd(1 1 1), was detected on the diffraction patterns of 3 wt.% Pt/ZrO_2 and 3 wt.% Pd/ZrO_2, respectively. Such observation would tend to indicate that Pt and Pd are not as well-dispersed on the support surface as the ruthenium is. Using Rietveld refinement, the average Pt and Pd crystallite size was estimated to be 40 and 18 nm, respectively. In conclusion, incipient-wetness impregnation was probably not the most appropriate preparation route to obtain well-dispersed Pt and Pd catalysts.

3.1.2. Specific surface area

The specific surface areas of the different catalysts are listed in Table 1. The surface area of the bare ZrO_2 support is

Table 1
Specific surface areas of the different materials

Catalyst	BET surface area ($m^2 g^{-1}$)
ZrO_2	90
3 wt.% Pt/ZrO_2	85
3 wt.% Pd/ZrO_2	84
3 wt.% Ru/ZrO_2	86

$90 \, m^2 \, g^{-1}$. After impregnation with 3 wt.% Pt, Pd or Ru, no significant modification is observed. As expected, the porous structure of the solid is not altered upon impregnation and reduction.

3.2. Catalytic performances

As part of a preliminary study described earlier [26], a blank experiment was carried out to examine the thermal stability of 2-CP. A 2-CP solution ($2 \, g \, L^{-1}$) was heated up to 413 K in the absence of any solid under Ar. No change in the TOC value was observed and only trace amounts of catechol and chlorohydroquinone were identified by HPLC. These results were consistent with previous reports [20,27] and indicated that 2-CP is thermally stable under the applied reaction conditions. Furthermore, we could conclude that (i) the stripping of the 2-CP molecule does not occur and (ii) the TOC removal at $t = 0$ can reliably be used to quantify the 2-CP adsorption on the solid surface.

3.2.1. CWAO of 2-CP over pure ZrO_2 and ZrO_2-supported noble metal catalysts

Fig. 2 shows the evolution as a function of time of the 2-CP conversion, the TOC removal and the pH upon the CWAO of a 2-CP aqueous solution ($2 \, g \, L^{-1}$) over pure and Pt, Pd, Ru loaded ZrO_2 at 413 K under 5 MPa (total pressure). It was found that ZrO_2 is only slightly active for the CWAO of 2-CP. Even after 24 h, the 2-CP conversion (30%) and the TOC removal (21%) are quite limited. In fact, taking into account the initial 2-CP adsorption on the zirconia support, ca. 15% as deduced from the TOC removal at time zero, the effective 2-CP conversion (15%) and TOC removal (7%) to be attributed to the bare support are very low.

Considering the TOC removal at zero time (Fig. 2b) on the different solids (between 13 and 18%), we came to the conclusion that 2-CP is mainly adsorbed on the support. After impregnation with 3 wt.% Pt, Pd or Ru, the catalyst activity is clearly modified. Among the noble metals we investigated, Ru appeared to be the best to promote the CWAO of 2-CP. Over 3 wt.% Ru/ZrO_2, a complete 2-CP conversion and a TOC removal up to 83% can be achieved after 8 h. In the case of Pt, the initial activity of the catalyst is very similar to Ru. The initial reaction rates over Ru/ZrO_2 and Pt/ZrO_2 are 6.7 and $6.3 \, mol_{2\text{-}CP} \, mol^{-1}_{metal} \, h^{-1}$, respectively. However, we must be cautious with such conclusion as far as the metal dispersion is clearly not the same for all catalysts. In fact, taking into account the metal dispersion, derived for the Rietveld refinement calculations, the initial activity of the Pt/ZrO_2 catalyst, expressed per square meter of metal exposed to the reactants, would be much higher than the one of Ru/ZrO_2. On the other hand, Pt appeared to be much less efficient for the degradation of the carboxylic acids which are formed upon the degradation of 2-CP and the reaction slows down significantly. Accordingly, the TOC abatement after 8 h of reaction over 3 wt.% Pt/ZrO_2 is only ca. 54%. The activity sequence would be Ru > Pt > Pd ≈ bare support ≈ 0. Then, as far as for real applications, the total mineralization of the CP molecule to CO_2 is absolutely required, without a sec-
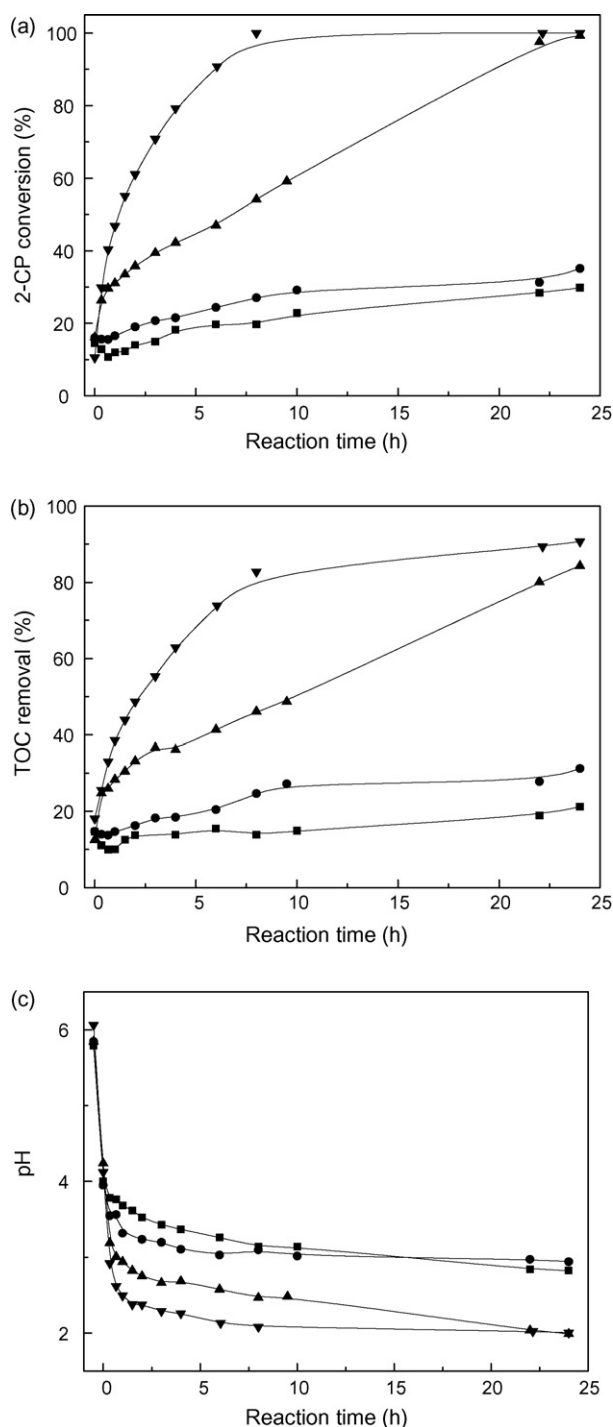
Fig. 2. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the catalytic wet air oxidation (CWAO) of 2-CP over ZrO_2 (■), 3 wt.% Pt/ZrO_2 (▲), 3 wt.% Pd/ZrO_2 (●), and 3 wt.% Ru/ZrO_2 (▼) [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [2-CP]$_0$ = 2 g L^{-1}].

ond treatment stage, Ru/ZrO_2 was chosen for the subsequent work.

Nevertheless, to conclude, further studies are required. The activity would have to be measured over catalysts with the same metal dispersion. For that, the preparation method of the different catalyst will not be uniform and would have to be adapted for each metal, especially Pt.

Moreover, the initial pH of the 2-CP solution was around 6 (Fig. 2c). At the very beginning of the reaction, the pH of the solution decreases sharply. The increase of the acidity is directly connected with the degradation of 2-CP and the production of HCl (2-CP dechlorination) [20]. The formation of acidic reaction intermediates would also contribute to a lower extent. From the analysis, small chain carboxylic acids such as acetic, chloroacetic and succinic acid could be identified. The formation of such acids is an indication that the degradation of 2-CP includes a ring cleavage. The fastest decrease is observed when Ru/ZrO_2 is used as a catalyst. In fact, a deeper oxidation is observed in the presence of Ru/ZrO_2. Consequently, a rapid measure of the pH might already give qualitative information about the degradation degree of the 2-CP molecule.

As reported in the literature [16,20], 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, especially at the initial reaction time. However, these intermediates were only present as traces and they could not be quantified. In any case, these by-products did not significantly account for the residual TOC. Further analysis, such as GC–MS, are under process to achieve the carbon mass balance in the liquid phase.

Finally, the selectivity to CO_2 (mineralization) might be expressed as the ratio TOC removal/2-CP conversion. Then, it appears that the selectivity is strictly higher than 78% all along the 24 h of reaction. Such a high selectivity indicates that most of the 2-CP is directly mineralized to CO_2, H_2O and HCl. In fact, after 24 h reaction over Ru/ZrO_2, 2-CP is nearly completely mineralized (91%) under the applied reaction conditions.

3.2.2. CWAO of CP over Ru/ZrO_2: effect of the position on the aromatic ring of the chlorine substituent

It is well-known that the position of any substituent on the aromatic ring may have an important effect on the physical and chemical properties of the molecule. As an example, the boiling point of 2-CP is lower than the boiling point of 3 and 4-CP. This is due to the possible intramolecular hydrogen bound between the Cl atom and the hydrogen from the hydroxyl group in the case of 2-CP that will limit intermolecular interactions. Such changes may indeed induce some modifications in the reactivity of the product. In the case of mono-chlorophenol, for example, 2-CP exists as a liquid at room temperature and atmospheric pressure, while 3-CP and 4-CP exist as solids. Furthermore, as far as the toxicity is concerned, the following sequence is reported in the literature: 4-CP > 3-CP > 2-CP [1].

In this work, in order to explore the universality of Ru/ZrO_2 for the CWAO of all mono-chlorophenols, the effect of the chlorine position on the aromatic ring (ortho, meta, para) on the performances of Ru/ZrO_2 was investigated. All tests were carried out under the same reaction conditions and the initial CP concentration was kept constant (2 g L^{-1}).

Fig. 3 shows the evolution as a function of time of the CP conversion and the TOC removal upon the CWAO of 2-CP, 3-CP and 4-CP over 3 wt.% Ru/ZrO_2. Generally speaking, Ru/ZrO_2 is very active in the CWAO of the three mono-chlorophenols. In all cases, a complete CP conversion and a TOC removal up to
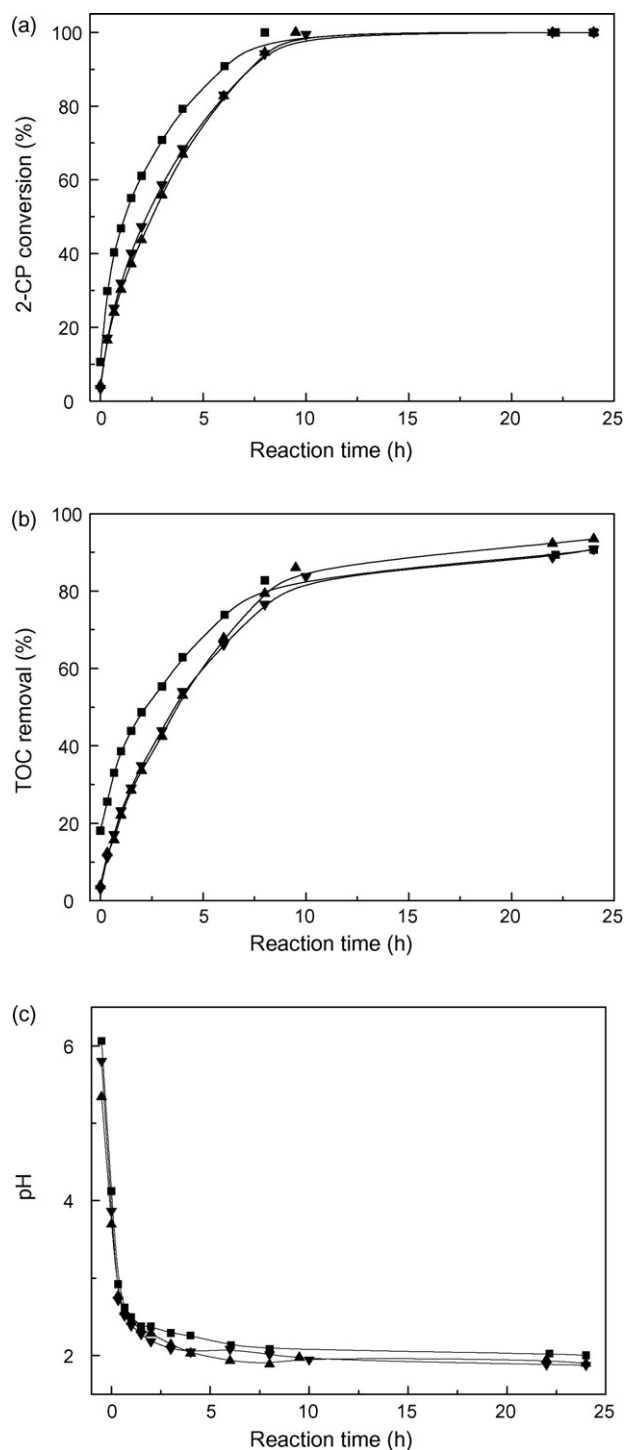
Fig. 3. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the catalytic wet air oxidation (CWAO) of 2-CP (■), 3-CP (▲), and 4-CP (▼) over the 3 wt.% Ru/ZrO$_2$ [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [CP]$_0$ = 2 g L^{-1}].

80% can be reached after 10 h of reaction. However, the 2-CP degradation is slightly faster than 3-CP and 4-CP. To a certain extent, this result could be tentatively explained by the different adsorption capacities of the different CP at the 3 wt.% Ru/ZrO$_2$ catalyst surface. In fact, the TOC removal at zero time (Fig. 3b) in the CWAO of 2-CP (18%) is clearly higher than the one observed

in the CWAO of 3-CP (4%) and 4-CP (3%). This means that 2-CP adsorbs much more strongly (in terms of adsorption capacity) on the Ru/ZrO$_2$ surface compared to 3-CP and 4-CP. The different pK_a of 2-CP, 3-CP and 4-CP (8.5, 9.0 and 9.4, respectively) could not be accounted for this behavior. However, this might tentatively be explained by the higher chelating effect of the 2-CP molecule compared to the other isomers, due to the position of the chlorine substituent relative to the hydroxyl group. Of course, the adsorption of 2-CP is probably not the unique reason for such behavior. Other parameters, such as the stability and the adsorption of the reaction intermediates may also be partly responsible for the higher reactivity of 2-CP.

Furthermore, inductive (electron donating/withdrawing) and mesomeric effects of the OH and Cl substituents on the aromatic ring (*o*-, *p*-directing/*m*-directing) should also be taken into account. However, further mechanistic studies would be required to analyze those effects accordingly.

Finally, the evolutions of the pH upon the CWAO of 2-CP, 3-CP and 4-CP are very similar (Fig. 3c). Such observation would tend to indicate that the catalytic degradation pathway is common to all mono-chlorophenol.

3.2.3. CWAO of 2-CP over Ru/ZrO$_2$: effect of the initial pH of the 2-CP solution

Considering the major role of the adsorption of the pollutant at the catalyst surface on the overall performances of the catalyst, as shown above, the impact of pH on (i) the catalyst adsorption properties (surface charging) and (ii) the speciation in the aqueous solution of the reactant and products was investigated.

The effect of pH on the efficiency and selectivity of the oxidation process was also evaluated in order to determine the optimum reaction conditions for the complete transformation and mineralization of the 2-CP molecule to harmless products.

Experiments were carried out with a 2 g L^{-1} 2-CP solution with initial pH 2.3, 8.0 and 10.1. To adjust the initial pH, H$_3$PO$_4$ or NaOH were used. The results obtained at pH 6.1, which is the natural pH of the solution (without any H$_3$PO$_4$ or NaOH addition), are also reported here for comparison purposes (dotted line). Reactions were performed using 3 wt.% Ru/ZrO$_2$ at 413 K under 5 MPa total pressure.

Fig. 4 shows the results. It appears that both the 2-CP conversion and the TOC removal increase when increasing the initial pH from 2.3 to 10.1. These results are similar to what has been found by Kojima et al. on Ru/TiO$_2$ [20]. In fact, the higher the pH, the faster the dechlorination of the 2-CP molecule (the faster the 2-CP conversion).

To discuss the adsorption properties of Ru/ZrO$_2$, the point of zero charge (pH$_{PZC}$) for the ZrO$_2$ support was determined using the method described by Brunelle [28]. The pH$_{PZC}$ for the ZrO$_2$ support we used in this study is 6.1. Below this pH, the zirconia surface would be positively charged and above this value, negative charges would be predominant at the catalyst surface. Additionally, the pK_a of 2-CP, acetic acid, chloroacetic acid and succinic acid (which are the main intermediates we identified) are 8.5, 4.8, 2.9 and 4.2, respectively. For a pH lower than the pK_a, the molecule would essentially exist in the undissociated
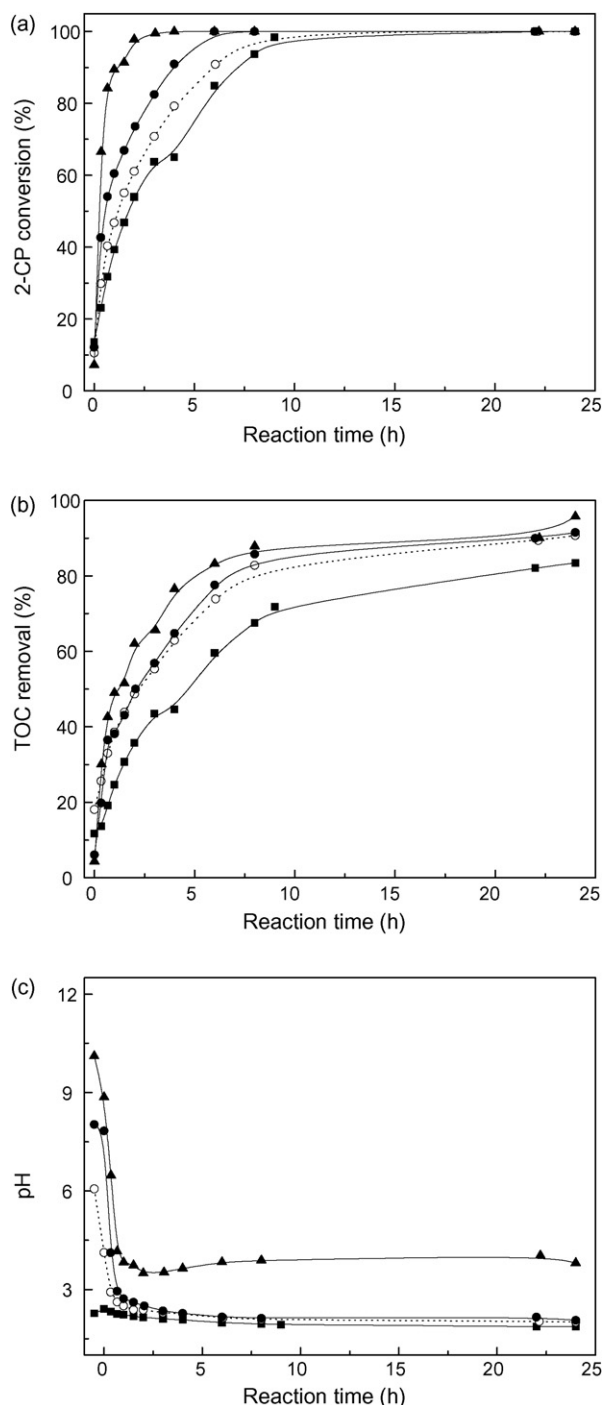
Fig. 4. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) in the CWAO of 2-CP over 3 wt.% Ru/ZrO$_2$ [0.5 g catalyst, 413 K, 5 MPa, 1300 rpm, [2-CP]$_0$ = 2 g L^{-1}, initial pH 2.3 (■), 6.1 (○), 8.0 (●), 10.1 (▲)].

form while for a pH higher than the pK_a, the anionic form(s) of the molecule predominate.

To start with, the fraction of the 2-CP molecules which is adsorbed on the catalyst surface was estimated by looking at the TOC removal values at zero time. When the initial pH is 2.3, 6.1, 8.0 and 10.1, the TOC removal at zero time is 12, 18, 6 and 4%, respectively. The initial 2-CP adsorption is maximum at pH equal 6.1. In fact, at such pH, the catalyst surface is about neu-

tral and no electrostatic barrier exists to prevent the adsorption of the 2-CP molecule. That sequence does not follow the activity sequence. In fact, the pH evolves very rapidly at the very initial time of the reaction and the adsorption equilibriums might rapidly be perturbed as the reaction proceeds. Additionally, the dechlorination reaction and the adsorption of the reaction intermediates are also potential key factors controlling the removal and the total mineralization of 2-CP.

Furthermore, when the starting pH is 2.3, the pH value stays below 3 all along the reaction. Under such pH conditions, the catalyst surface is positively charged and most reaction intermediates would be present in the undissociated form. Consequently, the adsorption of the intermediate products is limited (electrostatic barrier) and the reaction proceeds slowly.

On the opposite, at pH 10.1, the 2-CP molecule is initially in the chlorophenolate form. The pH rapidly evolves at the beginning of the reaction and stabilizes at pH around 4. In that case, the zirconia surface is positively charged and the main intermediates are present in the solution either as neutral species or in the anionic form. The adsorption of the main intermediates is somehow favored and the catalyst performances greatly improve.

At intermediate pH (6.1, 8.0), the situation is a little more complicated and a complete analysis of the catalyst performances would require to consider the possible interactions with the catalyst surface (adsorption) molecule after molecule. The explanations we gave here are only tentative ones. Further work is needed to get deeper insights on this reaction.

In conclusion, pH equal 10 might be considered as the optimum. However, from a practical and environmental point of view, the addition of important amounts of NaOH to the effluent might be difficult to work out. Consequently, in the following studies, the pH will remain unchanged at 6.1 which is the natural pH of the 2-CP solution.

3.2.4. CWAO of 2-CP over Ru/ZrO$_2$: effect of the total pressure

To test a little further the activity of Ru/ZrO$_2$, softer reaction conditions (lower temperature and/or lower pressure) were applied. We started by applying a lower total pressure.

The partial pressure of oxygen in the gas phase will partly determine the concentration of oxygen in the liquid phase. According to Henry's law, the concentration of O$_2$ dissolved in the liquid phase is proportional to the partial pressure of O$_2$ in the gas phase. At 413 K, the saturated vapor pressure for the water is 0.36 MPa. Furthermore, the argon pressure (from the purge of the solution at atmospheric pressure) is 0.14 MPa. Consequently, when the total pressure decreases from 5 to 3 MPa, the oxygen partial pressure decreases from 0.9 to 0.5 MPa. The oxygen solubility under such reaction conditions would be ca. 0.26 and 0.14 g L^{-1}, respectively.

The impact of the oxygen partial pressure on both the conversion and the mineralization of many organic pollutants upon CWAO was reported earlier [27,29–31]. As a general trend, it was observed that below 4 MPa, the lower the pressure, the lower the conversion and the mineralization. This effect was tentatively correlated to the oxygen availability at the catalyst surface.
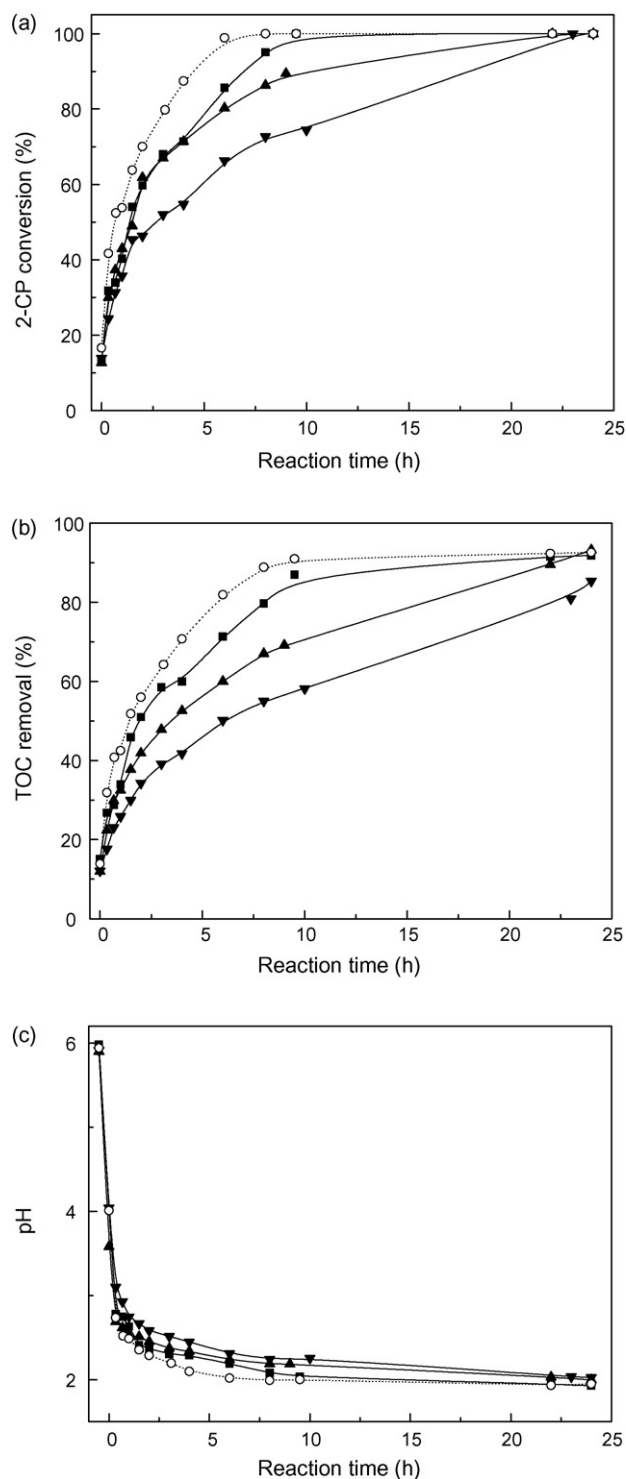
Fig. 5. Evolution of the 2-CP conversion (a), the TOC removal (b) and the pH (c) over the 3 wt.% Ru/ZrO$_2$ at 413 K, 5 MPa (○, dotted line); at 413 K, 3 MPa (■); at 393 K, 5 MPa (▲) or at 393 K, 3 MPa (▼) [0.5 g catalyst, 1300 rpm, [2-CP]$_0$ = 2 g L^{-1}].

Fig. 5 shows the evolution of the 2-CP conversion, the TOC removal and the pH upon reaction over 3 wt.% Ru/ZrO$_2$ at 413 K under 3 MPa or 5 MPa (dotted line). 3 wt.% Ru/ZrO$_2$ still exhibit high performances in the CWAO of 2-CP even when the total pressure is as low as 3 MPa. A complete 2-CP conversion and

TOC abatement higher than 87% can be reached after 9.5 h reaction.

3.2.5. CWAO of 2-CP over Ru/ZrO$_2$: effect of the reaction temperature

In a second step, we studied the impact of a lower reaction temperature (393 K versus 413 K). The reaction temperature is also expected to have a major impact on the CWAO of organic compounds. Three main effects might be identified: (i) according to Arrhenius' equation, the lower the reaction temperature, the slower the reaction; (ii) as reported in the literature, above ca. 373 K, the oxygen solubility in water decreases when the temperature decreases [32,33]; (iii) activation energies for the elimination of carboxylic acids, which ones are refractory to the oxidation, are high. It was calculated that the activation energy is 125 kJ mol^{-1} for the CWAO of succinic acid over Ru/TiO$_2$ [29] and 101 kJ mol^{-1} for the CWAO of acetic acid over Ru/C [34]. Consequently, a lower reaction temperature would mean a lower efficiency of the catalyst in the degradation of the intermediate carboxylic acids which are produced upon 2-CP degradation.

The performances of 3 wt.% Ru/ZrO$_2$ in the CWAO of 2-CP at 393 or 413 K (dotted line) under 5 MPa are reported on Fig. 5. Ru/ZrO$_2$ also exhibit high performances at lower temperature. Over 3 wt.% Ru/ZrO$_2$, a 2-CP conversion ca. 90% and a TOC removal ca. 70% can be achieved after 9 h reaction. This result further confirmed the high activity of Ru/ZrO$_2$ in the CWAO of 2-CP. The 2-CP mineralization (TOC abatement) is more sensitive to the reaction temperature than the 2-CP conversion. In fact, as the temperature decreases from 413 to 393 K, the reduction in the TOC abatement (20% after 10 h reaction) is much larger than the reduction in the 2-CP conversion (11% after 10 h reaction). It means in this case that an additional 9% of the 2-CP, which has been converted, has not been fully mineralized to CO$_2$, H$_2$O and HCl.

3.2.6. CWAO of 2-CP over Ru/ZrO$_2$: combined effect of the reaction temperature and the total pressure

Finally, we investigated the catalytic performances of Ru/ZrO$_2$ in the CWAO of 2-CP at lower temperature (393 K) and lower total pressure (3 MPa). High 2-CP conversion (74%) and TOC removal (58%) could still be achieved after 10 h. Even under such unprecedented and very middle reaction conditions, which are in turn very severe for the catalyst performances, complete 2-CP conversion and high TOC removal (ca. 85%) were obtained after 24 h reaction (Fig. 5).

4. Conclusions

It was demonstrated that Ru/ZrO$_2$ is an efficient catalyst in the CWAO of mono-chlorophenols. Over such catalyst, high 2-CP conversion and TOC removal could be reached at relatively low reaction temperature (393 K) and low pressure (3 MPa). Among the different mono-chlorophenols, 2-CP, which is more strongly adsorbed on the catalyst surface, was easier to degrade. Alkaline conditions were shown to favor the conversion of 2-CP by accelerating the dechlorination reaction. Finally, adsorption phenomena, which might be partly tuned depending on the reaction

conditions, were demonstrated to play a major role in the overall activity of the catalyst.

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