

# Reactivity of various Ru/CeO<sub>2</sub> catalysts during ozonation of succinic acid aqueous solutions

Nathalie Karpel Vel Leitner,\* Florence Delanoë, Benito Acedo and Bernard Legube

Laboratoire de Chimie de l'Eau et de l'Environnement (CNRS UPRES A 6008), Ecole Supérieure d'Ingénieurs de Poitiers, Université de Poitiers, 40 avenue du Recteur Pineau, 86022, Poitiers cedex, France. Fax: +33549453768; e-mail: Nathalie.Karpel@esip.univ-poitiers.fr

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Ozonation of aqueous solutions of succinic acid ([SA]<sub>0</sub> = 1 mM) was studied in the presence of ruthenium (2%) deposited on cerium dioxide catalysts. The influence of ruthenium, of the catalyst preparation mode (impregnation or exchange), of the support pretreatment, of the surface area and of the final treatment of the catalyst (by calcination or reduction) has been examined. Under our experimental conditions, the acid was not removed by ozone alone and its adsorption on the catalytic material was limited (< 120 µmol L<sup>-1</sup>). The presence of ruthenium was necessary for the observation of a catalytic activity of the cerium dioxide material. The best activity and mineralization are observed for the catalysts prepared by impregnation. Among the exchanged catalysts, the preparation using a basic exchange induces only a weak activity. Pretreatment of the support does not influence the catalytic properties whereas after Ru deposit, a final treatment by reduction is preferable to calcination. Such catalysts could be optimized in the future for their use in the field of wastewater depollution or even drinking water treatment.

**Réactivité de divers systèmes catalytiques Ru/CeO<sub>2</sub> lors de la réaction d'ozonation de l'acide succinique en milieu aqueux.** L'ozonation de solutions aqueuses d'acide succinique ([AS]<sub>0</sub> = 1 mM) a été étudiée en présence de catalyseurs constitués de 2% de ruthénium déposé sur du dioxyde de cérium. L'influence du métal, de son mode de dépôt (imprégnation ou échange), d'un prétraitement du support, de sa surface spécifique ainsi que d'un traitement final du catalyseur (par calcination ou réduction) ont été examinées. Dans des conditions où l'action de l'ozone seul conduit à une faible élimination de l'acide et où son adsorption sur le matériau est limitée (< 120 µmol L<sup>-1</sup>), il ressort que la présence de ruthénium sur le support est nécessaire pour obtenir un effet catalytique. Les catalyseurs préparés par imprégnation présentent une activité et conduisent à une minéralisation plus importante que les catalyseurs préparés par échange acide ou basique; ce dernier mode de préparation ne présentant qu'une faible efficacité. Si un prétraitement du support ne semble pas avoir d'influence sur les propriétés catalytiques, un traitement final par réduction est préférable à une calcination.

Oxidation processes are used in water treatment with various objectives: (i) removal of undesirable pollutants or micro-pollutants, (ii) improvement of biodegradability, (iii) carbon mineralization for water reuse or recycling. The classical processes used, including chlorine, chlorine dioxide or ozone, can lead to the removal of the compounds initially present but do not induce mineralization. The Advanced Oxidation Processes (AOPs) that involve the combination of oxidants and sometimes UV irradiation for the production of hydroxyl radicals (OH<sup>•</sup>) are now widely applied. Despite their high reactivity and low selectivity, these processes also yield refractory by-products. This refractory carbon is usually constituted by small carboxylic acids.

More recently, several laboratory studies focused on systems based on heterogeneous catalysis. These processes consist of catalytic wet air oxidation for concentrated solutions (> 1 g of carbon L<sup>-1</sup>)<sup>1,2</sup> and photocatalysis or catalytic ozonation for more diluted media (< 0.1 g of carbon L<sup>-1</sup>). The work presented in this article deals with the latter process.

The data relative to the ozonation of aqueous solutions in the presence of solid catalysts concern model molecules (pesticides, carboxylic acids, chloro aromatics) and surface waters. Generally the catalysts are constituted by metal oxides (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, etc.) alone or as supports for copper or cobalt, iron etc.<sup>3-13</sup> In most cases, the systems allowed a sig-

nificant improvement of the ozonation efficacy. Some studies carried out on wastewaters and leachates have shown that an interesting chemical oxygen demand abatement can be obtained by catalytic ozonation.<sup>3,14,15</sup> Several titanium dioxide or alumina catalysts introduced during the ozonation of natural organic matter from surface water were found to yield a better dissolved organic carbon removal than ozonation alone.<sup>5,6</sup> But the distinction between ozonation alone, adsorption and the catalytic effect was not always clearly described.

The experiments presented in this paper were performed on aqueous solutions of succinic acid (SA, HOOC(CH<sub>2</sub>)<sub>2</sub>COOH, pK<sub>a1</sub> = 4.16, pK<sub>a2</sub> = 5.61) with catalysts prepared from cerium dioxide and ruthenium. Succinic acid was selected due to its only slight reactivity with molecular ozone. In the literature,<sup>16,17</sup> cerium dioxide is considered as an interesting support for metallic ruthenium, used for the removal of organic acids in aqueous solution by the wet air oxidation process, which is performed under much more severe conditions.

The experimental conditions applied in our study enable us to highlight a large positive effect of the presence of these catalysts during ozonation with only low participating effects of adsorption and homogeneous ozonation. During ozonation, electronic exchanges could take place at the surface of

the catalyst and thus favor the oxidation reaction. These exchanges depend upon the mode of catalyst preparation. Therefore, the objective was to study the influence of the mode of catalyst preparation towards the removal of the initial compound and carbon mineralization during ozonation.

## Experimental

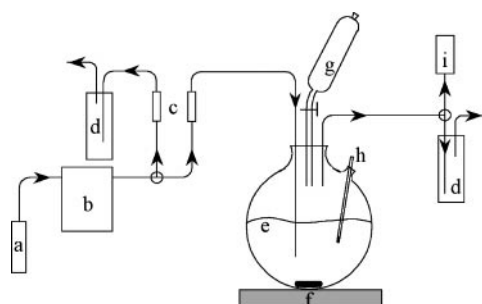
### Materials and methods

Experiments were performed at room temperature in a 500 mL reactor under semi-continuous flow conditions (Fig. 1). Ozone gas was generated from pure oxygen by a Trailigaz Labo 76 ozonizer and bubbled continuously into 250 mL aqueous solutions of succinic acid ( $[SA]_0 = 1 \text{ mM}$ ) through a fritted glass fitting.

Before starting the reaction, the powdered catalyst (200 mg) was first placed into the reactor. Then, the aqueous solution was introduced just before the ozone gas, which corresponds to the beginning of the reaction. The ozone flow rate was  $27.1 \pm 0.5 \text{ mmol O}_3 \text{ h}^{-1}$ .

The solutions ( $\text{pH}_0 = 3.4$ ) were prepared in unbuffered ultrapure water and stirred continuously during the reaction. Samples were withdrawn for analysis at different reaction times. Before SA and total organic carbon (TOC) analyses, the reaction was stopped by stripping residual ozone with nitrogen.

SA was analyzed by HPLC using a C610H column (Supelco) with an aqueous solution of phosphoric acid (0.1%) as eluent, and a photodiode array detector. Total organic carbon was measured with a carbon analyzer Dohrmann DC80. Dissolved ozone was analyzed by the carmine indigo method.<sup>18</sup>



**Fig. 1** Scheme of the laboratory-scale reactor used for the catalytic ozonation experiments: (a) oxygen gas, (b) laboratory ozone generator (Trailigaz), (c) gas flow-meter, (d) KI trap, (e) reactor, (f) magnetic stirrer, (g) funnel for solution introduction, (h) sampling, (i) thermal ozone destructor.

### Preparation of catalysts

Cerium dioxide (granulometry:  $50 \mu\text{m}$ , surface area:  $40$  or  $200 \text{ m}^2 \text{ g}^{-1}$ ) was used as support for all the catalysts. Various procedures were involved for ruthenium deposition and catalyst and support treatments (Table 1).

Cerium dioxide was used as received from the manufacturer (Rhône Poulenc, France) or after calcination and then reduction at  $500^\circ\text{C}$  with air and hydrogen, respectively. Ruthenium (2% weight) was then added by simple impregnation [with a solution of  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  followed by drying] or by specific impregnation, that is acid or basic exchange [with  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , respectively followed by filtration before drying]. These preparations are described in more detail in other studies.<sup>19</sup>

In most cases, except when indicated, the final treatment of the catalysts consisted in reduction with hydrogen ( $350^\circ\text{C}$ ), noted 2R/....

## Results and discussion

During catalytic ozonation, the removal of organic pollutants is either due to ozonation, adsorption, or catalytic oxidation. Since SA is not reactive towards ozone under our experimental conditions, as shown by Table 2, in accordance with literature ( $k_{\text{O}_3/\text{SA}} < 3 \text{ M}^{-1} \text{ s}^{-1}$  at  $\text{pH } 4\text{--}6$ <sup>20</sup>), our interest will be in adsorption and catalytic ozonation. Therefore, for each experiment, the evolution of the organic acid during ozonation in the presence of the catalytic material will be compared to the removal assigned to adsorption measured by replacing ozone by nitrogen.

### Impact of $\text{CeO}_2$ during ozonation

For the study of the efficiency of cerium dioxide as a catalyst for ozonation, two  $\text{CeO}_2$  materials were tested with surface areas of  $40$  and  $200 \text{ m}^2 \text{ g}^{-1}$ . In the presence of  $\text{CeO}_2$ , under nitrogen or ozone bubbling, a rapid decrease of the SA concentration is observed within the 2 min just after the introduction of the cerium dioxide. A plateau was then observed during the next 30 min showing an equilibrium. This evolution is similar under nitrogen or ozone and therefore this SA

**Table 2** Removal of SA in aqueous solution by ozonation alone (blank), by adsorption on  $\text{CeO}_2$  and by ozonation in the presence of  $\text{CeO}_2$  ( $[SA]_0 = 1 \text{ mM}$ ,  $\text{pH}_0 = 3.4$ ,  $27.1 \pm 0.5 \text{ mmol O}_3 \text{ h}^{-1}$ ). Influence of  $\text{CeO}_2$  surface area

% SA conversion at time/min	Blank	$\text{CeO}_2$ 200		$\text{CeO}_2$ 40	
	$\text{O}_3$	$\text{N}_2$	$\text{O}_3$	$\text{N}_2$	$\text{O}_3$
30	<4%	43%	43%	10%	10%
90	<4%	43%	68%	10%	12%

**Table 1** Description of the catalytic systems used for ozonation experiments

Name	Composition	Preparation	Treatment
$\text{CeO}_2$ alone	$\text{CeO}_2$ ( $40$ or $200 \text{ m}^2 \text{ g}^{-1}$ )	As received	None
2R/AE 200	$\text{CeO}_2$ ( $200 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Acid exchange	Final reduction at $350^\circ\text{C}$
2R/AE 40	$\text{CeO}_2$ ( $40 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Acid exchange	Final reduction at $350^\circ\text{C}$
2R/BE 40	$\text{CeO}_2$ ( $40 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Basic exchange	Final reduction at $350^\circ\text{C}$
2R/I 40	$\text{CeO}_2$ ( $40 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Impregnation	Final reduction at $350^\circ\text{C}$
2C/I 40	$\text{CeO}_2$ ( $40 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Impregnation	Final calcination in air at $350^\circ\text{C}$
2R/CRAE 40	Pretreated $\text{CeO}_2$ ( $40 \text{ m}^2 \text{ g}^{-1}$ ) Ru 2%	Calcination then reduction at $500^\circ\text{C}$ of the support before acid exchange	Final reduction at $350^\circ\text{C}$

removal can be assigned to adsorption. Similar results were also obtained by replacing nitrogen bubbling by oxygen (not presented).

The data in Table 2 show that:

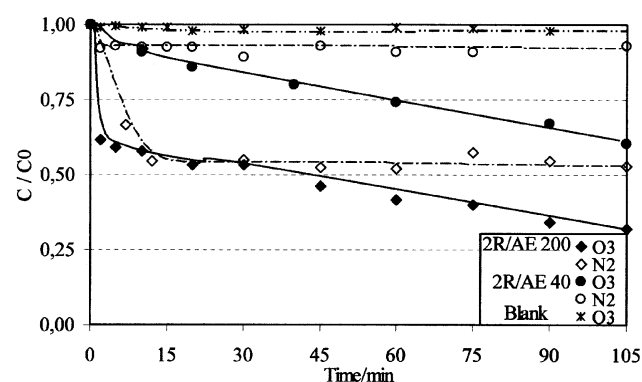
- (i) SA is weakly removed by ozone alone (<4%);
- (ii) SA is better adsorbed on the highest surface area  $\text{CeO}_2$  (10% for  $\text{CeO}_2$  40  $\text{m}^2 \text{g}^{-1}$  against 43% with  $\text{CeO}_2$  200  $\text{m}^2 \text{g}^{-1}$ );
- (iii) Ozone in the presence of the 40  $\text{m}^2 \text{g}^{-1}$   $\text{CeO}_2$  did not bring any significant improvement of the SA removal compared with the results obtained by adsorption under nitrogen.
- (iv) Activity was observed during ozonation with the 200  $\text{m}^2 \text{g}^{-1}$  cerium dioxide. After the rapid initial adsorption phenomena (43%), additional removal of SA (25%) was observed within the last 60 min of reaction.

### Catalytic behavior of metal supported systems

For all the following catalytic experiments,  $\text{CeO}_2$  was used as support for ruthenium. This metal was selected for our experiments since according to the literature and regarding the potential-pH diagram,<sup>21</sup> its leaching in the aqueous phase is limited. During our experiments the values of dissolved Ru were found to be less than 0.5% of the Ru brought by the catalyst.

**Acid exchanged Ru on  $\text{CeO}_2$ .** From the two  $\text{CeO}_2$  supports (40 and 200  $\text{m}^2 \text{g}^{-1}$ ), acid exchanged catalysts were prepared with 2% of ruthenium (2R/AE 40 and 2R/AE 200, respectively). For these two catalysts, Fig. 2 presents the evolution of SA concentration in solution during ozonation and nitrogen bubbling. In the presence of pure oxygen, the results were similar to those in the presence of nitrogen, and the SA removal is assigned to adsorption that is 10% for 2R/AE 40 and 43% for 2R/AE 200. These values are comparable to the supports without Ru,  $\text{CeO}_2$  40 and 200, respectively (Table 2). During ozonation, the 2R/AE 40 catalyst allows a significant improvement of SA removal compared with adsorption. This oxidation is not due to the action of oxygen contained in the ozonated gas. The evolution of the concentration of SA during catalytic ozonation is linear and the rates of SA conversion determined after the adsorption phase are 0.0034 and 0.0035  $\text{mmol mg}_{\text{cata}}^{-1} \text{min}^{-1}$  for 2R/AE 40 and 2R/AE 200, respectively. These values, which account for oxidation, do not depend on the cerium dioxide surface area, as opposed to the adsorption.

Thus, the behavior of the 2R/AE 200 catalyst as adsorbent of the organic molecule (0.430  $\text{mmol L}^{-1}$  of SA) is important compared with the oxidative action. Under our experimental conditions, the additional catalytic effect due to the presence of Ru, in contrast to 2R/AE 40, is not significant for 2R/AE



**Fig. 2** Influence of cerium dioxide surface area on the removal of SA ( $C/C_0$ ) by adsorption and during ozonation with Ru/ $\text{CeO}_2$  catalysts prepared by acid exchange (AE). ( $[\text{SA}]_0 = 1 \text{ mM}$ ,  $\text{pH}_0 = 3.4$ ,  $27.1 \pm 0.5 \text{ mmol O}_3 \text{ h}^{-1}$ ).

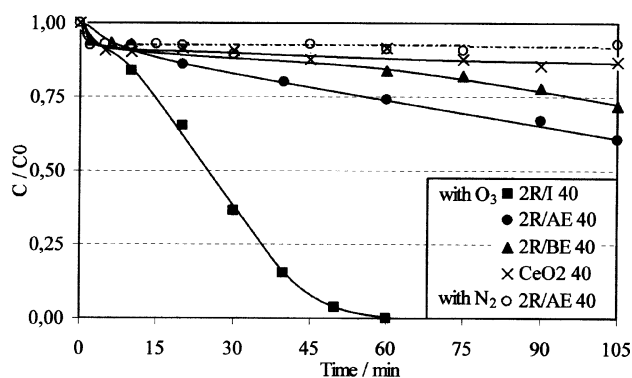
200 (70% removal of SA after 90 min under an ozone stream vs. 68% without Ru). To consider mostly the catalytic activity and to limit the contribution of adsorption, the following experiments will be performed with the catalyst supported by the 40  $\text{m}^2 \text{g}^{-1}$  cerium dioxide.

**Influence of the metal deposition mode.** The amphoteric properties of cerium dioxide (isoelectric point: 6.25) enables the preparation of basic exchanged catalysts, 2R/BE 40, in addition to acid exchanged catalysts (2R/AE 40). For the study of the influence of the metal deposition mode, the third preparation used was impregnation. These various preparations involve various electronic interactions between the metal and the support. The exchange preparation induces a more important distribution of the Ru particles.<sup>19</sup>

Experiments with nitrogen bubbling have shown that the adsorption is not influenced by the preparation procedures of these catalysts. Fig. 3 indicates that the conversion of SA by catalytic ozonation is more important in the presence of the catalyst prepared by impregnation than in the presence of the exchanged catalysts. Up to 60 min of reaction, only a small difference was found between the catalytic effect of the 2R/BE 40 catalyst and the  $\text{CeO}_2$  40 support. The rates of succinic acid conversion are respectively: 0.029, 0.004, 0.002 and  $<0.001 \text{ mmol mg}_{\text{cata}}^{-1} \text{min}^{-1}$  for 2R/I, 2R/AE, 2R/BE and  $\text{CeO}_2$  40.

Concerning their efficiency towards TOC abatement, Table 3 presents for the three Ru catalysts the yield  $\eta = ([\text{TOC}]_0 - [\text{TOC}])/([\text{SA}]_0 - [\text{SA}])$ .

A  $\eta$  value close to zero indicates a small mineralization of SA whereas total removal of the oxidation by-products is reached when  $\eta$  is equal to 1. Table 3 shows that the  $\eta$  values of the three catalysts vary with ozonation time. For the 2R/I 40 and 2R/BE 40 catalysts, the  $\eta$  values are small at the beginning of the ozonation and then increase with time. For the 2R/I 40 catalyst, 92% of the initial TOC is removed after 60 min of ozonation, corresponding to the total removal of SA.



**Fig. 3** Influence of catalyst preparation mode on the removal of SA during catalytic ozonation ( $[\text{SA}]_0 = 1 \text{ mM}$ ,  $\text{pH}_0 = 3.4$ ,  $27.1 \pm 0.5 \text{ mmol O}_3 \text{ h}^{-1}$ ).

**Table 3** Dissolved ozone (in  $\text{mmol L}^{-1}$ ) and TOC removed (expressed as  $\eta$ ) in the catalytic ozonation of SA for different Ru/ $\text{CeO}_2$  catalysts (experiments of Fig. 3)

Ozonation time/min	2R/AE 40		2R/I 40		2R/BE 40	
	$\eta$	$[\text{O}_3]$	$\eta$	$[\text{O}_3]$	$\eta$	$[\text{O}_3]$
10	0.74	0.19	0.36	0.15	0.17	0.18
30	0.88	0.20	0.52	0.06	0.37	0.19
45	0.81	0.21	0.86	0.06	0.52	0.19
60	0.65	0.21	0.92	0.10	0.56	0.19

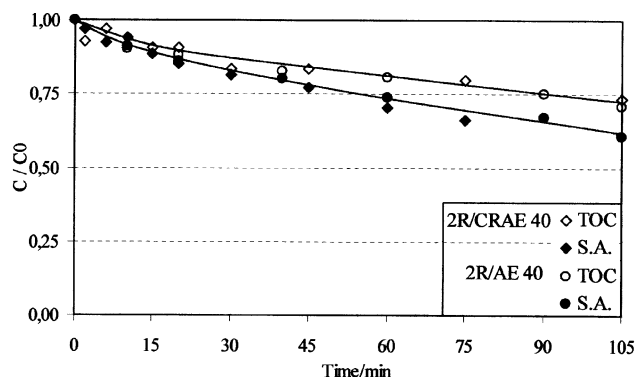


Fig. 4 Catalytic ozonation of SA with acid exchanged catalysts prepared from calcinated then reduced or raw  $\text{CeO}_2$  material; ( $[\text{SA}]_0 = 1 \text{ mM}$ ,  $\text{pH}_0 = 3.4$ ,  $27.1 \pm 0.5 \text{ mmol O}_3 \text{ h}^{-1}$ ).

The 2R/BE 40 catalyst presents a small efficacy not only towards the removal of SA but also towards the by-products ( $\eta < 0.6$ ). Contrary to the other catalysts, it appears that the 2R/AE 40 catalyst does not require an important initiation period since the  $\eta$  value reaches 0.74 in first 10 min of ozonation and then increases to 0.88. The subsequent decrease may be due to saturation of some active sites and accumulation of refractory by-products. The different evolutions observed with these various catalysts probably arise from different mechanisms. Nevertheless, even if the TOC abatement is close to the SA removed with the 2R/AE 40 catalyst, for the ozonation times used in this study, the efficiency remains limited.

Analyses of dissolved ozone showed that the concentration does not evolve significantly during the reaction in the presence of the 2R/AE 40 and 2R/BE 40 catalysts (Table 3). These values were found to be close to  $0.20 \text{ mmol L}^{-1}$ , which is below the value obtained without catalyst ( $0.34 \text{ mmol L}^{-1}$ ). For the 2R/I 40 catalyst, dissolved ozone concentration decreases during the oxidation of SA. For this catalyst, the ozone concentration seems to be linked to the catalytic efficiency. The concentration increase, observed after 45 min of ozonation could be an indication of the completion of the reaction. Regarding the stable concentration of dissolved ozone measured during the oxidation with the exchanged catalysts, their activity is not limited by ozone. Despite a smaller dissolved ozone concentration, the Ru catalyst prepared by impregnation yields a better SA conversion than the exchange preparations.

The preparation technique using impregnation usually induces a different distribution of the metal than the specific impregnation by exchange preparations and could result in different interactions with ozone involving different mechanisms. For the two catalysts, 2R/AE 40 and 2R/I 40, the percentage of Ru is similar (2%). Moreover, the two preparation modes yield the same ruthenium particle size and consequently the same number of sites. A ruthenium particle size of 3.5 nm was found during the characterization of these

catalysts, presented in another publication.<sup>19</sup> Therefore, it seems that the rate of catalytic ozonation is rather connected to the accessibility of these sites, which depends on the catalyst preparation, rather than their number.

**Influence of support pretreatment.** In addition to the study of the influence of the preparation mode, the influence of the catalyst treatment can be useful to better understand the catalytic ozonation process. The interactions between the metal and the support depend on the functional groups of the latter. The influence of calcination and reduction of the cerium dioxide at  $500^\circ\text{C}$  before contact with Ru was examined for the catalyst prepared by acid exchange. The results of the catalytic ozonation experiments presented in Fig. 4 indicate that this pretreatment has no effect on the catalyst efficiency. It appears that the support pretreatment does not influence the metal distribution during the exchange step of the catalyst preparation.

**Effect of final reduction vs. calcination of Ru catalysts.** The purpose of the final treatment of the catalysts after metal deposition is to ensure chemical bonds and to fix the oxidation states of the catalyst surface. For comparison with the classical final treatment by reduction, a calcination with air at  $350^\circ\text{C}$  of the Ru impregnated catalyst was studied. The ozonation experiments performed on these two catalysts showed that the preparation consisting of a final treatment by reduction is preferred to calcination (Fig. 5). Reduced metal is favorable to the catalytic ozonation. Moreover, these results indicate that if small amounts of ruthenium were present in solution, they would probably not induce significant SA removal. They would be rapidly converted by ozone to the oxidized form of ruthenium, which is found to be unreactive.

## Conclusions

The reactivity of succinic acid in an aqueous solution at pH 3.4 is small with ozone alone but can be greatly increased in the presence of catalysts consisting of cerium dioxide with 2% by weight of ruthenium. The study of the activity of this catalytic material prepared by different techniques (impregnation, acid or basic exchange, pre- and post-treatments) showed that a final treatment by reduction is preferable to calcination and that the impregnated catalysts are more efficient than the exchanged ones. In addition to succinic acid removal, an interesting TOC abatement is achieved. Therefore, the reactions induced by catalytic ozonation are assumed to depend on the nature of the interactions between the support and the metal and on the oxidation degree of the latter: reduced metal with a localized distribution is preferred. Characterization of the catalysts during the catalytic ozonation is now necessary for an understanding of the mechanisms involved in the process.

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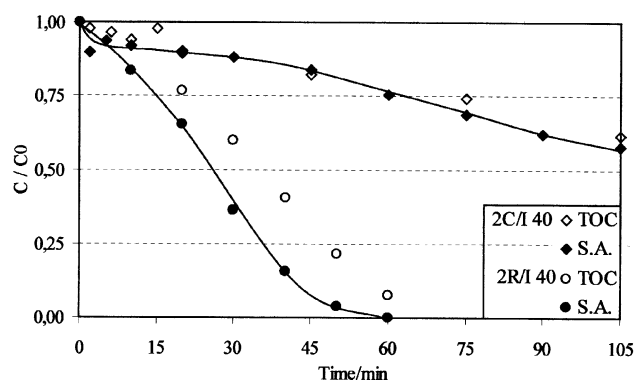


Fig. 5 Influence of final treatment of the impregnated catalyst.

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