Catalytic ozonation: a promising advanced oxidation technology for water treatment

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Abstract

The first part of this paper presents generalities on molecular ozone reactivity. The second part focuses on catalytic ozonation with the objective to evaluate the efficiency of such an AOT versus ozonation alone. The literature data relative to catalytic ozonation concerns either the activation of ozone with metals in solution, or the heterogeneous behavior of solid catalysts. Numerous metals (Fe, Mn, Ni, Co, Zn, Ag, Cr) under various forms (salt of reduced metal, solid oxide, deposited metal on support) were reported to enhance the efficiency of ozone towards the removal (or the conversion) of different organic compounds in aqueous solution. Some years ago, heterogeneous catalytic ozonation has begun to be studied in our group. This paper presents a short synthesis of the main results obtained, illustrated by three different experimental procedures which can be used to test catalytic ozonation. Finally, some hypothesis on reaction mechanisms and prospects are examined. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Ozone; Catalyst; Aqueous solution; Organics oxidation; Water treatment

1. Introduction

Except for some European countries where ozone is already currently used for drinking water treatment, interest in the use of ozone has been steadily increasing over the last several years for drinking water treatment in all countries in the world. Since the early nineties, new regulations on chlorine disinfection and chlorination by-products are expected to further increase the drinking water industry’s interest in this technology. However, the recently discovered problem of bromate, as ozonation by-products in drinking water treatment, could finally decrease the predicted development of ozone in this field.

As far as the main chemical properties of ozone are concerned, numerous data have been already published. Many books present complete synthesis of literature on this subject [1–4]. It is now widely assumed that ozone reacts in aqueous solution on various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical induced by the ozone decomposition in water (Fig. 1). Ozone decomposition proceeds with chain reactions including initiation steps, propagation steps and chain breakdown. The fundamental role played by the hydroxide ions in initiating the ozone decomposition process in water is well known. In fact a wide variety of compounds are able to initiate (i.e. hydrogen peroxide, humics, reduced metals, formate), to promote (i.e. primary and secondary alcohols, humics, ozone itself) or to inhibit
(i.e. tertiary alcohols, carbonate) the radical chain reaction.

As for treatment of industrial wastewater, many researches were led to further improve the efficiency of ozonation for various applications. Ozone in alkaline solution ($O_3 + OH^-$), photolysis of ozone ($O_3/UV$), perozone ($O_3 + H_2O_2$), catalytic ozonation are the principal existing (or future) AOTs known as the most promising processes for industrial effluents depollution.

The first part of this article presents generalities about molecular ozone reactivity in order to give some background to the reader unspecialized in the field of ozone, and some bases for the final discussion about mechanism hypotheses. The second part focuses on catalytic ozonation. Its objective is to evaluate the efficiency of a such AOT versus ozonation alone, with the help of a literature review including our own works. In the conclusion, some hypotheses on reaction mechanisms and prospects are examined.

2. Summarized background on ozone and OH$^*$ radical reactivities

2.1. Reaction of molecular ozone with reduced metals

Second-order rate constants for the reaction of molecular ozone with a great number of inorganics (more than 50) are reported in the literature, mainly by Hoigné and Bader [5]. Some of them are very reactive whatever the pH (such as sulfite, sulfide, nitrite ions) be, some others exhibit a low rate constant in acidic medium and a significant increase of their reactivity as pH increases (like hypochlorous acid, hypobromous acid, ammonia). Iron (II) and manganese (II) which are present in natural waters can be quickly oxidized by ozone into insoluble oxides easily removed by filtration. As for Fe(II) oxidation by ozone, a first mechanism has been proposed by Hart [6]. As shown in the Fig. 2, it consists of an electron transfer from the reduced metal to ozone, forming Fe(III) and the radical ion $O_3^-$, then the OH radical. In the presence of an excess of Fe(II), the OH radical can oxidize a second Fe(II) finally leading to a stoichiometric ratio of 0.5 mol of ozone per mol of ferrous iron.

More recently, Nowell and Hoigné [7] maintain that the hydroxyl radical is not an intermediate in the reaction of Fe(II) with ozone and assume a mechanism involving an oxygen-transfer from ozone to ferrous iron (Fig. 2).

As far as we know, no study was published on the mechanism of reaction of ozone with other reduced transition metals such as copper or cobalt, nor with noble metal such as ruthenium.

2.2. Reaction of molecular ozone and OH radicals with organics

Rate constants for the reaction of ozone with non-dissociating organic compounds (aliphatics, alcohols, olefins, chlorosubstituted ethylenes, substituted benzenes, polyaromatics, carbohydrates, etc.) and dissociating organic chemicals (amines, aminoacids, carboxylic acids, phenols, etc.) are reported in literature [8,9]. The second-order rate constants are in the range from $10^{-2}$ to $10^9$ M$^{-1}$ s$^{-1}$ and increase with pH as does the degree of deprotonation of the organics (some examples are given in Table 1). All results support the electrophilic nature and the selectivity of reactions of molecular ozone, either by 1–3 dipolar cycloaddition or by electrophilic substitution.
Table 1  
Ozonation rate constants [8,9] and OH rate constants [10] for some organic compounds

<table>
<thead>
<tr>
<th>Solute</th>
<th>$k_{O_3}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{OH}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$2 \pm 0.4^a$</td>
<td>$7.8 \times 10^9$</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>$0.99 \pm 0.02^a$</td>
<td>$3.9 \times 10^9$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$14 \pm 3^a$</td>
<td>$3.0 \times 10^9$</td>
</tr>
<tr>
<td>$m$-xylene</td>
<td>$94 \pm 20^a$</td>
<td>$7.5 \times 10^9$</td>
</tr>
<tr>
<td>Formic acid</td>
<td>$5 \pm 5^a$</td>
<td>$1.3 \times 10^8$</td>
</tr>
<tr>
<td>Formate ion</td>
<td>$100 \pm 20^b$</td>
<td>$3.2 \times 10^7$</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>$(&lt;4 \times 10^{-2})^a$</td>
<td>$1.4 \times 10^6$</td>
</tr>
<tr>
<td>Oxalate ion</td>
<td>$(&lt;4 \times 10^{-2})^b$</td>
<td>$7.7 \times 10^6$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$(&lt;3 \times 10^{-5})^a$</td>
<td>$1.6 \times 10^7$</td>
</tr>
<tr>
<td>Acetate ion</td>
<td>$(&lt;3 \times 10^{-5})^b$</td>
<td>$8.5 \times 10^7$</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>$(&lt;3 \times 10^{-2})^a$</td>
<td>$3.1 \times 10^8$</td>
</tr>
<tr>
<td>Succinate ion</td>
<td>$(&lt;3 \times 10^{-2})^b$</td>
<td>$3.1 \times 10^8$</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>$&lt;500^a$</td>
<td>$2.2 \times 10^{10}$</td>
</tr>
<tr>
<td>Salicylate ion</td>
<td>$(3 \pm 3) \times 10^3^b$</td>
<td>$1.6 \times 10^{10}$</td>
</tr>
</tbody>
</table>

$^a$ Acidic pH, in the presence of OH$^\cdot$-scavenger.  
$^b$ In the presence of OH$^\cdot$-scavenger.

Ozonation alone has been shown to achieve a very limited mineralization of organic compounds concerning micropollutants removal in drinking water treatment or removal of refractory COD in industrial effluents. Consequently, various advanced oxidation processes or AOPs (such as O$_3$/H$_2$O$_2$, UV/O$_3$, UV/H$_2$O$_2$, Fenton and UV/Fenton reagents, photocatalytic oxidation with TiO$_2$, WAO and WPO processes, electron beam, catalytic ozonation) have been investigated as potential methods for degrading organic compounds.

A common objective of the AOPs is to produce a large amount of radicals (especially OH$^\cdot$) to oxidize the organic matter. Indeed, hydroxyl radical is a less selective and more powerful oxidant than molecular ozone, as shown by some rate constants given in the Table 1, withdrawn to the review of Buxton et al. [10]. The three main mechanisms involved are: H abstraction, OH addition or substitution and electron transfer. Abstraction of hydrogen atom is often the first step of the oxidative pathway of aliphatic acids by OH radicals [11].

3. Catalytic ozonation as an advanced oxidation technology: a brief literature review

Recently, alternative ozonation processes catalysed by transition metals have been investigated for degradation of organics. Literature data relative to catalytic ozonation can be classified according to (i) activation of ozone by metals in solution and (ii) heterogeneous catalytic ozonation in the presence of metal oxides or metals on supports.

3.1. Activation of ozone by metals in solution

Hewes and Davinson [12] have shown that the presence of Fe(II), Mn(II), Ni(II) or Co(II) sulfate during ozonation of wastewaters induces an increase of TOC removal as compared to ozonation alone.

Zinc or copper sulfate, silver nitrate and chromium trioxide were shown by Abdo et al. [13] to catalyse the bleaching of dye effluents during ozonation.

More recent investigations were conducted by Garcia et al. [14,15] who showed that in the presence of Mn and Ag, ozonation of humic substances in water allows an important reduction in the content of organic matter as compared to ozonation alone.

Andreozzi et al. [16] found that Mn(II) accelerates the oxidation of oxalic acid under acidic conditions. Consistent with the previous statement from Nowell and Hoigné [7] that no production of OH radicals can be directly derived from the transition metals ozonation, the authors proposed that Mn(II)-catalysed oxidation was proceeding through complexing between oxalic acid and Mn(III), forming an intermediate product which might be easier oxidized by ozone (Fig. 3).

3.2. Heterogeneous catalytic ozonation

Al-Hayek et al. [17] have shown that ozonation of phenol in the presence of the catalyst Fe(III)/Al$_2$O$_3$ leads to a significant increase of the TOC removal as compared to ozonation alone. The authors suggested either a formation of free radicals or an increase of nucleophilic sites of adsorbed molecules.
Bhat and Gurol [18] studied the ozonation of chlorobenzene in the presence of goethite and found that catalytic ozonation was more effective than ozonation alone.

Naydenov and Mehandjiev [19], and Thompson et al. [20] observed a mineralization of benzene and 1,4-dioxane, respectively, in aqueous solution, obtained by ozonation in the presence of MnO2.

Ma and Graham [21] have shown that MnO2 formed in situ by ozonation of atrazine in the presence of small amounts of Mn(II) leads to a much greater degree of atrazine oxidation compared to ozone alone. The authors assigned these results to the generation of highly oxidative intermediate species.

Andreozzi et al. [22] reported a significant improvement of oxalic acid ozonation at acidic pH, induced by the presence of MnO2.

Pines et al. [23] stated that the combination O3/metal-TiO2 was particularly interesting for the oxidation of hydrophilic (biodegradable) compounds. However, the efficiency was found to be weak for hydrophobic compounds.

Volk et al. [24] studying fulvic acid oxidation by O3, O3/H2O2 and O3/TiO2 found that catalytic ozonation induced a smaller BDOC formation than the other two processes and deduced that carboxylic acids (ozonation by-products) could be oxidized preferably by catalytic ozonation.

Finally, numerous experiments were carried out at the University of Poitiers in collaboration with a French water Company [25–27]. Some of these results are presented below.

4. Some selected results demonstrating the efficiency of catalytic ozonation

Various experimental procedures have been applied to evaluate the efficiency of solid catalysts in the presence of dissolved ozone in water. These methods consist of batch or semi-continuous tests, on the one hand, and in filtration experiments for the continuous tests, on the other. The results presented below illustrate these three experimental procedures using different solid catalysts either provided by companies or prepared by ourselves. The objectives consisted in: applied research for drinking water treatment, applied research for recycling of rinse waters from metal finishing facilities, and fundamental research.

4.1. Organics removal for drinking water treatment using transition metals as catalysts, in batch reactor [27]

At the beginning of our works, the objective was to evaluate the efficiency of catalytic ozonation to remove organics for drinking water treatment.

The fresh catalytic materials (supplied by a water company) were composed of copper impregnated on three different supports: alumina (300 m²/g, 10 wt.% Cu), anatase (61 m²/g, 5 wt.% Cu) and attapulgite (59 m²/g, 5 wt.% Cu). Solutions of organic compounds (2.5–3 mg/l as total organic carbon or TOC) were prepared in deionized water (milli-Q milli-RO water) containing sodium carbonate and calcium chloride to simulate natural water (alkalinity = 250 mg/l as CaCO3, ionic strength = 1.3 × 10⁻² M, pH = 7.2). The batch reactor was a 60 ml flask stopped with a tight septum containing 6 g of either support or catalyst and 46 ml of the test solution. Ozonation was carried out with a rapid injection of a small volume of ozonated water (containing 50 mg O3 per liter) through septum with a syringe. After 10 min-stirring, ozone in gas phase and solution and total organic carbon were determined as described previously [27].

In order to quantify the catalytic effect as compared with ozonation alone, an ozone dose of 2.2 to 2.5 mg O3/mg of TOC was applied. Moreover, the adsorption of organic compounds on the catalyst was roughly evaluated. Each experiment was performed six to eight times at room temperature in the dark. The Fig. 4 presents the results obtained from solutions of aquatic humic substances (previously extracted from a natural water) and salicylic acid (as model compound).

They show that ozonation performed without catalyst (in the conditions summarized above) leads to a low TOC removal (12–15%). Moreover, humic substances and salicylic acid are adsorbed on the alumina and anatase based-catalysts and catalytic ozonation does not always improve significantly the TOC removal (especially in the case of humic substances). However, considering the attapulgite-based catalyst, adsorption of initial organic compounds appears negligible and catalytic ozonation (Clay-Me, Fig. 4) was...
found to improve the TOC removal as compared to ozonation alone.

4.2. Organics removal for recycling of rinse waters from metal finishing facilities, using transition metals as catalysts, in batch and continuous-flow reactors

Surface treating and metal facilities involve a variety of process baths for cleaning operations. These process baths containing complexing agents and surfactants are followed in downstream by several rinse stages containing pure water. The objective of catalytic ozonation here is to try to remove organic impurities (gluconate ion, p-tolune-sulfonic acid, triethanolamine, etc.) in rinse water in order to reuse this water. Two different experimental procedures have been applied to test the efficiency of catalysts supplied by a manufacturer participating in the global project (project co-financed by the European Commission under the Brite-Euram). Different types of catalysts have been used, transition metals impregnated on zirconia-alumina support, on the one hand, and cogel type catalyst with same components, on the other. Solutions of organics were prepared in unbuffered deionized water (milli-Q milli-RO water). Analytical methods for organic compounds, organic and inorganic carbon and ozone were presented previously [28].

Batch test experiment: firstly, a batch test procedure was used to quickly evaluate the efficiency of catalytic ozonation towards selected molecules and TOC removal (Fig. 5). Ozonation experiments were performed by adding (under stirring) 58 ml of a stock solution of dissolved ozone in deionized water (at a concentration between 14 and 22 mg/l of ozone) to 1 ml of a concentrated solution of the organic compound. Analyses were then performed after a given contact time (\(t_1\) on Fig. 5). As for adsorption test, 3 g of (each) selected catalyst were added to the ozonated solution where residual dissolved ozone was previously quenched with \(\text{Na}_2\text{S}_2\text{O}_3\) after a \(t_1\) period of time. The mixture was stirred again during a second period of time (\(t_0\)) before sampling for analyses. As for the catalytic ozonation test, 1 ml of concentrated solution of organic compound was diluted with 58 ml of the same ozone stock solution in the presence of 3 g of catalysts, and stirred during the same period of time (\(t_1\)) as during ozonation alone. Note that, contrary to the first series of experiments (presented above), this new batch procedure allows to compare catalytic ozonation and ozonation alone with adsorption of ozonated solution (that is to say adsorption of initial compound plus ozonated by-products).

The effect of the contact time value (\(\Delta t\)) has been studied with p-toluene sulfonic acid (TOLS). Data are presented in the Table 2, in mg/l of organic carbon in order to make easy the comparison between TOLS and the TOC remaining in solution. These data show: (i) in spite of a large change in the concentration of TOLS, ozonation of TOLS was found to lead to a weak TOC abatement, (ii) TOLS was not really adsorbed on the catalyst but the formed ozonation
Fig. 5. Experimental procedure for catalytic ozonation batch tests ($\Delta t = \Delta t'$) with $p$-toluene sulfonic acid.

Table 2
Catalytic ozonation efficiency compared with ozonation plus adsorption and ozonation alone for $p$-toluene sulfonic acid in batch conditions (presented in Fig. 6). TOLS $\sim$ 100 $\mu$M (in deionized water, pH $\sim$ 4). Catalyst: metal transition on zirconia-alumina as support

<table>
<thead>
<tr>
<th>Contact time (min)</th>
<th>Catalytic ozonation</th>
<th>Ozonation plus adsorption</th>
<th>Ozonation alone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOC (mg C/l)</td>
<td>TOLS (mg C/l)</td>
<td>Ozone (mg/l)</td>
</tr>
<tr>
<td>0</td>
<td>7.9</td>
<td>8.1</td>
<td>16.9</td>
</tr>
<tr>
<td>5</td>
<td>5.9</td>
<td>3.8</td>
<td>10.1</td>
</tr>
<tr>
<td>10</td>
<td>5.6</td>
<td>3.1</td>
<td>8.1</td>
</tr>
<tr>
<td>20</td>
<td>4.0</td>
<td>2.9</td>
<td>3.2</td>
</tr>
<tr>
<td>30</td>
<td>3.1</td>
<td>1.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

By-products were significantly adsorbed (3.3 mg/l of remaining TOC are due to ozonation by-products after 30 min of ozonation, 40% can be adsorbed by the catalyst under the experimental conditions), (iii) catalytic ozonation yielded an improvement towards both TOLS and TOC removal (TOC removal by catalytic ozonation almost twice as that by ozonation plus adsorption), (iv) the ozone consumption was found to be significantly improved by the catalyst. Other experiments with TOLS and other organics were performed in order to compare various catalysts. The results have been presented elsewhere [28].

Continuous flow experiment: in the same study, a continuous flow reactor (presented in Fig. 6) was used in order to get a carbon mass balance. Aqueous solution of organic compound (5 mg/l as C) in deionised water was ozonated in the ‘bubble’ column in the following conditions: solution input and output flow rate = 1.9 l/h, contact time = 10 min, ozone gas flow rate = 950 mg/h, temperature 20–40°C. As for catalytic ozonation experiment, to avoid technical difficulties linked to a three phases system, 5 g of catalysts (selected above) were located in a recirculating flow circuit (35 l/h) and therefore in contact only with the
solution containing dissolved ozone and, of course, organics. Solution samples were taken at the output of the ‘bubble’ column for analyses of dissolved ozone, aqueous carbon dioxide, pH, TOC and organics. Except for the determination of ozone in off-gas, the gas outlet was connected to the washing-flask containing a solution of NaOH (1 g/l) to trap the carbon dioxide arising from mineralization of organics. As for ozonation experiment, the procedure was the same, inert glass balls replaced catalyst.

The Table 3 presents some results obtained with TOLS (initial concentration = 59 μM or 5 mg C/l) at different temperatures (20, 30 and 40°C) after 3–5 h of running in the continuous flow reactor. These data show: (i) whatever the temperature be, some amounts of carbon (organic or inorganic) remain adsorbed on catalyst, (ii) at 20°C, it is impossible to conclude about the efficiency of catalytic ozonation versus ozonation, (iii) at more elevated temperature a significant improvement of TOLS conversion into CO₂ was found and allowed to demonstrate the catalytic effect. Other experiments were performed, more especially on identification and evolution of some organic by-products, namely pyruvic, acetic and formic acid.

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**Table 3**

Oxidation of p-toluene sulfonic acid by ozonation and catalytic ozonation, in a continuous flow reactor (presented in Fig. 7) TOLS = 59 μM (in deionized water, pH = 4). Catalyst: metal transition on zirconia-alumina as support.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catalyst</th>
<th>% TOC remaining</th>
<th>% IC a produced</th>
<th>% C adsorbed on catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Without</td>
<td>88.2</td>
<td>11.8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>With</td>
<td>83.1</td>
<td>7.6</td>
<td>9.3</td>
</tr>
<tr>
<td>30</td>
<td>Without</td>
<td>84.3</td>
<td>15.7</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>With b</td>
<td>69.1</td>
<td>26.0</td>
<td>4.9</td>
</tr>
<tr>
<td>40</td>
<td>Without</td>
<td>67.9</td>
<td>32.1</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>With</td>
<td>44.5</td>
<td>41.6</td>
<td>13.9</td>
</tr>
</tbody>
</table>

a IC: inorganic carbon in solution plus off-gas.

b Average of two experiments.
Pyruvic and formic acids were found to be less present during catalytic ozonation as compared to ozonation alone, while acetic acid was highly produced by catalytic ozonation.

4.3. Succinic acid removal: a fundamental approach (still in progress), using noble metals as catalysts, in semi-continuous reactor

In order to get a better control and knowledge of the catalyst preparation and activity, we decided more recently to evaluate the capability of catalytic ozonation from catalysts prepared by ourselves. The molecule chosen for this study was succinic acid which is a refractory compound towards ozone alone (Table 1). Experiments were carried out in a semi-continuous flow reactor (Fig. 7) where ozone gas (prepared from pure oxygen) was bubbling continuously into a 250 ml-aqueous solution of succinic acid (0.5–2 mM) prepared in unbuffered deionised water (milli-Q-milli-RO water) at pH 3.4. Each set of experiments consisted in: (i) catalytic ozonation, with 1250 mg O3/h in the presence of 50–300 mg of catalyst, (ii) ozonation alone, with 1250 mg O3/h in the absence of catalyst, (iii) adsorption of succinic acid on the catalyst, under oxygen bubbling in the presence of 50–300 mg of catalyst. All catalysts were made of ruthenium and cerium oxide (50 m2/g, 40 or 200 m2/g, calcinated then reduced at 350°C). Ruthenium was added (2% weight) either by impregnation (Ru(NH3)6Cl3) or by acid (RuCl3) or basic (Ru(NH3)6Cl3) exchange. The catalysts obtained were then either oxidized in an air flow or reduced in a hydrogen flow, both at 350°C. Aqueous samples were withdrawn at different ozonation times for organics and dissolved ozone analysis [29].

The Fig. 8 presents the preliminary experiments, carried out twice, with a reduced catalyst prepared by acid exchange on 200 m2/g – CeO2. Results show that (i) ozonation was found to have no effect on succinic acid conversion (as expected), (ii) adsorption of succinic acid on the catalyst (in the presence of an oxygen flow) was found to be not very important (an apparent equilibrium was reached after 30 min), (iii) after the adsorption phase, the catalytic ozonation was found to be really effective for a large amount of ozone applied.

Other tests with three different catalysts (prepared from 40 m2/g – CeO2) have shown that the reduced impregnated catalysts were preferred to reduced acid or basic-exchanged catalysts. Finally, the influence of the final treatment of the catalyst by calcination or reduction (after ruthenium deposit) was examined. Results presented on the Fig. 9 demonstrate that reduction of catalysts under hydrogen flow (at 350°C) induces a significant improvement of the global conversion of succinic acid.

5. Discussion

The whole literature relative to catalytic ozonation is focused on the activation of ozone by numerous metals (Fe, Mn, Ni, Co, Zn, Ag, Cr) in solution or by heterogeneous catalysts with metals under various forms (salt of reduced metal, solid oxide, deposited metal on support). It was concluded that these metals
are able to enhance the efficiency of ozone for the removal (or the conversion) of different organic compounds in aqueous solution. However, to our knowledge, not many satisfactory hypothesis of mechanism have been given in these works.

Some years ago, heterogeneous catalytic ozonation has begun to be studied in our laboratory. This paper presents a short synthesis of the main results obtained, illustrated by three different experimental procedures which can be used to test catalytic ozonation.

Using batch test procedures, it was demonstrated that catalysts (prepared by impregnation or by the cogel technique) with given transition metals on various oxides (alumina, anatase, zirconia, clay), can really improve ozonation efficiency and oxidize some polar compounds such as salicylic acid, tripeptide, aquatic fulvic acid and p-toluene sulfonic acid. However, adsorption of such organics on oxides is often too strong to demonstrate clearly the real action of the catalysts (except for clay) and, hence, it was difficult in these experimental conditions, to determine the mass balance between the remaining organic carbon in solution and on solid and the carbon dioxide produced by oxidation.

Using a continuous reactor designed to evaluate the formed carbon dioxide, it was shown that a small amount of catalyst located in the reactor can increase the mineralization of organics as compared to ozone alone. This effect was found to increase with the temperature increase (between 20 and 40°C).

Finally, since the catalysts used in these studies were supplied by companies and then subject to a minimum of confidentiality, some further experiments were recently carried out with a catalyst prepared by ourselves (from ruthenium and cerium oxide) on succinic acid (which is not reactive towards molecular ozone) in pure aqueous solution, with large applied ozone doses. Of course, these experimental conditions are not realistic (catalyst is expensive, succinic acid is not currently found in water and wastewater to be treated), but they allowed us to highlight a large positive effect of the presence of catalyst during ozonation with only low participating effects of adsorption and homogeneous ozonation. Moreover, it was shown that the catalysts prepared by the impregnation mode achieve a higher global conversion of succinic acid than the exchanged catalysts, and that a reduction treatment improves the activity of the impregnated catalysts as compared with the calcination treatment.

As for mechanisms occurring in catalytic ozonation, we can propose two main possibilities. In the first one, the catalyst would behave only as adsorbant (Me-OH, Fig. 10a); ozone and hydroxyl radical would be the oxidant species. Firstly, initial organic acid (AH, Fig. 10a, i.e. salicylic acid or succinic acid) would be quickly adsorbed on the support of catalyst. It is known that some oxides, especially alumina [30], are able to form surface chelate rings with bidentate ligands (such as salicylic and oxalic acids). Consequently a strong negative charge would appear into the six or five-membered chelate ring at the surface, and ozone (or hydroxyl radical) would then oxidize the surface complex to give oxidation by-products either desorbed in solution (P₀ and R₀: primary and final by-products, respectively, Fig. 10a) or still adsorbed at the surface of catalyst (P and R: adsorbed primary and final by-products, respectively, Fig. 10a). The final adsorbed by-product (R, Fig. 10a) would desorb and thereafter be oxidized in homogeneous solution by ozone or hydroxyl radical. In this hypothesis the real role of the deposit metal (copper, ruthenium, etc.) is not clear and support alone should be responsible for the improvement of ozonation. Although the presence of supports only were found to enhance ozonation in some cases (especially with alumina), this mechanism is probably not important with low adsorbing supports such as clay and cerium dioxide.
In the second mechanism, the catalyst would react with both ozone and adsorbed organics, that is to say would behave as a true catalyst. Starting to the reduced catalyst (Me_{red}, Fig. 10b), ozone would oxidize metal. Note that this first step could be deciding, because it was shown here that a reduction pretreatment applied to the ruthenium-based catalyst before use, leads to a more operative material than a calcination pretreatment. The reaction of ozone on reduced metal could lead to OH radical in accordance with the reaction of ozone with Fe(II) as proposed in literature [6]. Organic acids (AH, Fig. 10b) would be adsorbed on oxidized catalyst and then oxidized by an electron-transfer reaction to give again reduced catalyst (Me_{red}A^*, Fig. 10b), similarly to the scheme proposed for the Mn(II)-catalysed ozonation of oxalic acid [16]. The organic radical species A^* would be then easily desorbed from catalyst and subsequently oxidized by OH or O_3 either in bulk solution, or more probably, into the thickness of electric double layer. In some cases, adsorption and diffusion of organics at the surface of the catalyst would be the limiting step, as shown by some of our results with ruthenium-based catalysts [29] and new results still in progress. In other cases, such as catalysts made with copper and clay, elevated concentrations of OH produced by the reaction of ozone with copper, at the solid–liquid interface, could be mainly responsible for the improvement of ozonation induced by the presence of catalysts.

6. Conclusion

In spite of the increasing number of data demonstrating the efficiency of catalytic ozonation, a better
knowledge in various fields is still needed as far are concerned:

The fundamental aspects (mechanisms of reaction of ozone with reduced metals, identification and quantification of oxidation by-products in solution and at the surface of catalyst, study of the effect of some reaction parameters such as pH, temperature, presence of radical scavenger), or more practical aspects (study of the life-time of catalyst, engineering design and economic study).

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