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Kinetics and mechanism of catalytic ozonation of aqueous pollutants on metal oxide catalysts

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Abstract

The catalytic ozonation of fenofibric and clofibric acids and the herbicides atrazine and linuron was studied using titanium dioxide, alumina, and manganese oxide supported on activated alumina and on silica SBA-15. The organics studied did not adsorb significantly either in wastewater or in phosphate-buffered water. The catalysts did not modify the rate of the hydroxyl-mediated ozonation with respect to the homogeneous value. The mode of action of metal oxide catalysts would be an enhanced generation of oxidant species from the catalytic decomposition of ozone. All catalysts increased the efficiency in the production of hydroxyl radicals from ozone.

Keywords: ozone, catalytic ozonation, fixed bed, titanium dioxide, manganese oxide, hydroxyl radicals.

1. Introduction

Ozonation processes have been proposed for the removal of wastewater pollutants (Beltrán, 2004). In this regard, the discharge of Wastewater Treatment Plants (WWTP) has been shown to be the major responsible factor for the introduction of anthropogenic pollutants into the aqueous environment (Ternes, 1998). The removal of these compounds and their metabolites, and the study of toxicity evolution associated with effluent and treatment, are key issues in current research (Petrovic et al., 2004; Rosal et al., 2009a).

Ozone is known to be a powerful oxidant, but it reacts slowly with some organic compounds such as inactivated aromatics. As a consequence, it does not lead to the complete oxidation of organics, which results in the formation of carboxylic acids, carbonyl compounds and many others. In recent years, catalytic ozonation has been attracting the interest of the scientific community dedicated to the study of ozone processes in water treatment due to the enhancement of the production of hydroxyl radicals and the corresponding ozone economy (Kasprzyk-Hordern et al., 2003). Activated carbon has been used as ozonation catalyst to take advantage of its high adsorption capacity and its ability to transform ozone into hydroxyl radicals, which can further degrade adsorbed and dissolved organic compounds (Álvarez et al., 2009).

Recently, the use of carbon nanotubes has attracted considerable attention because they are more resistant to degradation than activated carbon (Liu et al., 2008). Metal oxide catalysts can improve ozone reactions in aqueous solutions and also provide a high stability and the possibility of using a number of active phases and surface modifications (Kasprzyk-Hordern et al., 2003). Catalytic ozonation can be performed using catalysts dispersed within the liquid phase or in the form of solid either suspended or in fixed bed. The use of three-phase beds for heterogeneous catalytic ozonation has been reported in connection with granular activated carbon or metal oxides supported on it (Ma et al., 2005). Fixed bed reactors offer the advantage of a high catalyst-to-liquid ratio, which may limit parallel-undesired reactions leading to oxidation by-products.

In spite of the considerable research in the field of catalytic ozonation performed during recent years, the mechanism of catalytic processes is still essentially unknown. It has been demonstrated that several catalysts enhance the efficiency of ozonation, but a deeper knowledge of this process is required prior to introduce this technique to water treatment on an industrial scale.

There are two major gaps in understanding catalytic ozonation. First, it is not completely clear whether catalysts cause ozone decomposition, leading to the formation of hydroxyl radicals, although some recent papers using electron paramagnetic resonance showed that metal oxides accelerated the generation of hydroxyl radicals during ozonation (Yang et al., 2007). On the other

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hand, there is still no direct evidence of ozone adsorption on metal oxides in the presence of water and whether the decomposition of ozone leads or not to the formation of surface-bound radicals or other surface oxidizing species (Nawrocki and Kasprzyk-Hordern, 2010).

Finally, it is not known whether the adsorption of organics on the surface of catalyst plays a role in the process. Certain authors reported high adsorption of organic molecules on catalysts, but the presence of salts and other competing compounds makes it difficult to assess the importance of the adsorption of organic molecules during the catalytic ozonation of real streams. The goal of this work was to determine whether the interaction between organic compound and catalytic surface may lead to an energetically favoured pathway. Furthermore, this study aimed to determine the influence of MnO_x on the increase of hydroxyl radicals produced from ozone and the effect of a greater surface dispersion of the oxide when using SBA as support instead of activated alumina.

In this work, we report the results of several ozonation studies performed using different polar and non-polar compounds typically encountered in wastewater. This includes the lipid regulators clofibric and fenofibric acid and the herbicides atrazine and linuron. Among them, only the oxidation of atrazine was previously studied by means of catalytic ozonation (Guzman-Pérez et al., 2011; Tepuš and Marjana, 2007). We used different matrices including a real wastewater and phosphate-buffered pure water with different ionic strengths. The purpose was to determine whether the adsorption of organics may result or not in an interaction with the catalytic surface of metal oxides that could lead to an energetically favored pathway. We also tried to determine whether the catalyst increased the generation of hydroxyl radicals from ozone.

2. Theoretical background

The rate of ozonation of an organic compound in an ozonation process is a consequence of its second-order parallel reaction with dissolved ozone and with hydroxyl radicals. Elovitz and von Gunten (1999) assumed that the ratio of the concentration of hydroxyl radicals and ozone is a parameter that represents the efficiency of the system in generating hydroxyl radicals. We determined thereafter that R_{ct} may be constant during the ozonation of wastewater and in general in the presence of matrices with a high concentration of radical scavengers (Rosal, Rodríguez et al., 2010). The overall rate of depletion of a given compound "A" is:

$$\begin{aligned} r_A\left(mol\,L^{-1}\,s^{-1}\right) &= k^h_{O_3}\,c_A\,c_{O_3} + k^h_{HO\bullet}\,c_A\,c_{HO\bullet} \\ &= \left(k^h_{O_3} + k^h_{HO\bullet}\,R^h_{ct}\right)c_A\,c_{O_3} \end{aligned} \qquad [1]$$

The superscript "h" indicates homogeneous (non-catalytic) reaction. In heterogeneous ozonation, the activity of a solid catalyst may be due to any of the following mechanisms: (i) adsorption of organics on the solid surface with reaction with oxidized surface sites or adsorbed oxidant species; (ii) reaction of non-adsorbed organics from the bulk with oxidized surface sites or surface-adsorbed oxidants; (iii) reaction of organics adsorbed on the surface of the catalysts that react with the ozone of hydroxyl radicals from the bulk; and, (iv) reaction taking place in the bulk, the activity of the catalyst being based on an enhanced generation of oxidant species through the catalytic decomposition of ozone.

In the presence of a solid catalyst, the rate of ozonation might be (mechanisms i to iii) the result of another parallel process, namely the oxidation of organics by surface-oxidized sites or adsorbed hydroxyl radicals on the catalyst surface. In a previous article, we showed that the rate of catalytic ozonation in the presence of t-BuOH 10 mM, a well-known radical scavenger, was not significantly different from that of the homogeneous process indicating that the direct ozonation reaction is not a catalysed process (Rosal, Gonzalo et al., 2010b). As a consequence, the rate of the catalysed process would be as follows:

$$r_A\left(mol\,kg^{-1}\,s^{-1}\right) = \frac{k^c_{HO\bullet}\,R^{hc}_{ct}\,c_A\,c_{O_3}}{\left(1+K_A\,c_A\right)\left(1+K_{ox}\,c_{O_3}\right)} \qquad [2]$$

where K_{ox} is the equilibrium constant for the reaction yielding adsorbed oxidizing species or oxidized surface sites and K_A the adsorption equilibrium constant for the organic compound. Assuming surface equilibrium and low surface coverage, the rate expression for catalytic ozonation becomes linear with the concentration of adsorbate and ozone:

$$r_A\left(mol\,kg^{-1}\,s^{-1}\right) = k^c_{HO\bullet}\,R^{hc}_{ct}\,c_A\,c_{O_3} \qquad [3]$$

The superscript "hc" stresses the fact that catalysed and uncatalyzed reactions must take place simultaneously. The competition method used atrazine as reference compound. As the hydroxyl radical-to-ozone ratio is the same for all compounds in the reaction mixture, the following expression can be derived:

$$\ln\left(\frac{c_{Ao}}{c_A}\right)=\frac{k^{h}_{O_3(A)}+k^{hc}_{HO\bullet(A)}\,R^{hc}_{ct}}{k^{h}_{O_3(ATZ)}+k^{hc}_{HO\bullet(ATZ)}\,R^{hc}_{ct}}\;\ln\left(\frac{c_{ATZo}}{c_{ATZ}}\right) \qquad [4]$$

In this expression, the concentration of catalyst in suspended bed and bed porosity and bed bulk density are used to transform pseudo-homogeneous (mol L^{-1} s^{-1}) into heterogeneous (mol kg^{-1} s^{-1}) units. Assuming that all compounds are exposed to the same concentration of hydroxyl radicals or surface oxidants:

$$k^{hc}_{HO\bullet}=k^{h}_{HO\bullet}+k^{c}_{HO\bullet} \qquad [5]$$

The ratio of the logarithmic concentration decay between a certain compound and the reference neutral compound atrazine is a parameter that can be experimentally determined as a function of the hydroxyl-to-ozone ratio, R^{hc}_{ct}:

$$m=\frac{k^{h}_{O_3(A)}+k^{hc}_{HO\bullet(A)}\,R^{hc}_{ct}}{k^{h}_{O_3(ATZ)}+k^{hc}_{HO\bullet(ATZ)}\,R^{hc}_{ct}} \qquad [6]$$

The hydroxyl-to-ozone ratio has been experimentally determined from the concentration profile of atrazine using data from ozone concentration sampled every 5 s. It was assumed that, being atrazine a neutral compound that does not significantly adsorb on any of the catalysts studied in this work, its rate constant $k^{hc}_{HO\bullet}$ should equal the homogeneous value $k^{h}_{HO\bullet}$ found elsewhere (Balci et al., 2009).

3. Materials and methods

All chemicals were high-purity analytical grade reagents supplied by Sigma–Aldrich. The wastewater used for spiking was collected from the secondary clarifier of a WWTP located in Colmenar Viejo (Madrid) that operates with a conventional activated sludge treatment for a maximum volume of wastewater of 8000 m^3 day^{-1}. The main characteristics of this wastewater are COD 83 mg L^{-1}, TOC 14.3 mg L^{-1}, bicarbonate 115 mg L^{-1}.

The heterogeneous catalysts used in this study were TiO_2, Al_2O_3, MnO_x/Al_2O_3 and MnO_x/SBA-15. TiO_2 Degussa P25, a mixture 80/20 of anatase/rutile with primary particles of about 20 nm that form larger aggregates up to several hundred nanometers. The point of zero charge (PZC) of this catalyst was 6.6 as already reported (Rosal et al., 2008) and its BET specific surface was 52 ± 2 m^2 g^{-1} determined by nitrogen adsorption at 77 K. γ-Al2O3, specific surface area 155 m^2 g^{-1} and particle size 100 μm, was purchased from Sigma–Aldrich and used as received. Alumina supported manganese oxide, MnO_x/Al_2O_3, was prepared by incipient wetness impregnation of the aforementioned dried Al_2O_3 using an aqueous solution of $Mn(CH_3COO)_2{\bullet}4H_2O$ (Sigma-Aldrich). The catalyst was subsequently dried in air at 423 K and calcined at 773 K for 3 hours. The amount of manganese corresponded to a 10% wt. of MnO_2 and its BET surface area was 119 m^2 g^{-1}. Mesoporous MnO_x/SBA-15 was prepared by the impregnation of silica SBA-15 obtained as follows. Pluronic P123 (Aldrich $EO_{20}PO_{70}EO_{20}$ (EO: ethylene oxide, PO: propylene oxide) and tetraethoxysilane (TEOS 98% Aldrich) were used as received In a typical synthesis, 6 g of Pluronic P123 were stirred at 308 K in 45 mL of water and 180 mL of 2 M HCl solution until total dissolution. TEOS (12.5 g) was added to the solution and stirred at 308 K for 20 hours. The mixture was aged at 373 K for 24 hours. The white powder was recovered through filtration, washed with water, and dried at 323 K overnight. The product was calcined at 773 K for 12 hours with a heating rate of 1 K min^{-1}. The impregnation of the SBA-15 was carried out by the minimum volume method. In a typical impregnation the desired amount of manganese precursor, Manganese nitrate tetrahydrate (Fluka) 2.01 g was dissolved in 30 mL of water and the solution poured slowly over 5 g of calcined SBA-15 while being stirred for 10 hours. The solid was dried at 323 K overnight and activated under at 773 K for 12 hours. The prepared catalysts presented 12% wt. of MnO_2 and had a particle size of 1.3 ± 0.2 μm as determined by Dinamic Light Scattering in a Malvern Zetasizer instrument. BET surface area was 650 m^2 g^{-1}. Pore size distribution has been calculated using the Broekhoff and de Boer (BdB) method and showed a narrow peak distribution around 5 nm. PZC was obtained by measuring the ζ-potential in aqueous solutions at 25ºC and at various pH values after adjusting ionic strength to 10-3 M with NaCl. The value of PZC for MnO_x/Al_2O_3 as prepared was 7.3, which fell to 3.0 after contact with bubbling ozone in aqueous slurry for 30 min. For MnO_x/SBA-15 the surface was almost neutral, with a ζ-potential of -1.3 ± 0.8 mV at pH 6.5 that became negatively charged after contact with bubbling ozone. The decrease of ζ-potential could be attributed to the production of negatively charged surface oxygen-containing groups and may be relevant for explaining the interaction with organics or with ozone. All catalysts were stabilized in PBW under ozone flow prior to use.

Semicontinuous ozonation runs were performed in a glass-jacketed reactor whose temperature was controlled at 20 ºC using a thermostatic regulator. pH was controlled at the desired value within ±0.1 units by means of a feed-back control device that delivered a solution of sodium hydroxide through a Shimadzu pump. Alternatively, certain runs were performed in solutions adjusted to pH 6.5 using phosphate buffered water (PBW), usually 0.1 M. Ozone was produced by a corona discharge ozonator (Ozomatic, SWO100) fed by an AirSep AS-12 PSA oxygen generation unit which produced a flow of 1.8 g/h of ozone.

The gas containing ozone was continuously bubbled throughout the run. In certain runs, we added t-BuOH at different concentrations (67 µM, 1.0 mM and 10 mM), in order to inhibit or suppress the contribution of the radical reaction. In the samples withdrawn for analysis, dissolved ozone was removed by adding sodium thiosulfate or by bubbling nitrogen at a flow-rate of about 0.2 $Nm^3\ h^{-1}$. The kinetics depends on the relative rates of physical absorption and chemical reaction. The kinetic regime of a gas–liquid ozonation process is determined by the Hatta number, which represents the maximum rate of chemical reaction relative to the maximum rate of mass transfer. In all cases, we ensured that all results corresponded to the slow kinetic regime ($Ha < 0.4$), a conclusion confirmed by a criterion based on the appearance of ozone in solution explained in a previous work (Rosal, Rodríguez et al., 2010). Additional details are given elsewhere (Rosal, Gonzalo et al., 2009a, 2010a; Rosal, Rodríguez et al., 2008).

We also performed runs using a fixed bed reactor fed by PBW loaded with ozone solution. In order to avoid the complexity of gas-liquid-solid reactions, we used a two-phase heterogeneous catalytic device operating in excess of ozone. The concentration of ozone in the stock tank varied in the 5.0–10.0 mg L^{-1} range according to the desired dose for each run. The ozone solution was delivered to the reactor at a flow-rate of 2.0–4.5 mL min^{-1} using a HPLC Shimadzu pump. The solution containing organics was delivered to the upper part of the catalytic bed using a Harvard Dual Syringe Pump, which also pumped a quenching agent that stopped reaction immediately after leaving the column. PVDF tee connectors ensured the absence of back-mixing and excessive dead volumes. The catalysts tested in the fixed bed device were Al_2O_3, MnO_x/Al_2O_3 and MnO_x/SBA-15. Details on the experimental set-up are given elsewhere (Rosal, Gonzalo et al., 2010b).

In semicontinuous runs the catalyst was pre-oxidized prior to the reaction for 15 min with the same ozone flow as that used for ozonation. In fixed-bed runs the catalyst was preconditioned with ozone for at least 2 h before performing the first measurement. By periodically checking with reference conditions, no loss of efficiency or deactivation could be measured for any of the catalytic beds used in this work during their service period.

4. Results and discussion

Fenofibric and clofibric acids, whose pK_a are 2.9 and 3.2, respectively, dissociate in aqueous solution even under acidic conditions. It has been demonstrated that the adsorption of dissociated acids may take place on metal oxides at pH < pHPZC as their surface can behave as an anion exchanger. We observed adsorption extents up to typically 10–15% but only in pure water and with very slow kinetics in comparison to that of ozonation reactions (Rosal, Gonzalo et al., 2009b).

Either in water containing phosphate (PBW) or in spiked wastewater we never could measure any adsorption significantly different from zero after 24 h contact time and using any of the organics mentioned before. Neutral compounds, namely atrazine and linuron, were not adsorbed to any significant extent, even when dissolved in pure water. These results indicate that the interaction of the surface of metal oxides with dissolved organic compounds is weak and probably does not lead to a transition state involving the reaction with adsorbed organics.

It has been clearly stated, however, that both TiO2 and MnO_x accelerate the decomposition of dissolved ozone (Rosal, 2010a; Rosal, Rodríguez et al., 2006). On the other hand, and in spite of the lack of adsorption of organics, our results show a positive effect of the catalysts on the degradation of all compounds tested as indicated in Figure 1, which shows the concentration of clofibric and fenofibric acids and atrazine during several catalytic and non-catalytic ozonation runs as a function of integral ozone exposure. The adsorption of organics on catalytic ozonation processes has been usually invoked in the mechanism proposed for catalytic ozonation on metal oxides, which assumes that the adsorption of both organics and ozone takes place simultaneously on the surface of the catalyst (Logemann and Anne, 1997).

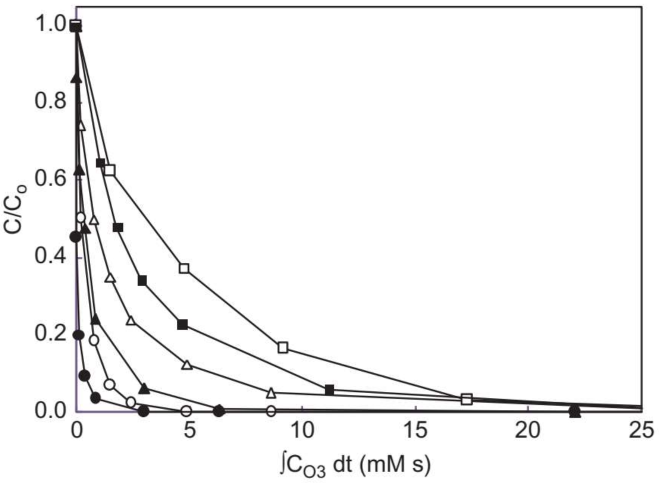

Figure 1. Relative concentration of clofibric acid (□, ■), fenofibric acid (○, ●) and atrazine (Δ, ▲) during catalytic (filled symbols) and non-catalytic (empty symbols) ozonation runs as a function of integral ozone exposure. The catalysts used were MnO_x/Al_2O_3 for atrazine and fenofibric acid and TiO_2 for clofibric acid. Reaction conditions: pure water at pH 5 for clofibric acid and PBW at pH 6.5 for atrazine and fenofibric acid with a catalyst concentration of 1 g/L.

Kasprzyk-Hordern et al. (2003) underlined the need for considering the adsorption properties of metal oxides when discussing their catalytic activity, particularly concerning dissociated substances that could be affected by ion-exchange with charged surfaces. More recently, some data pointed oppositely, and Yang et al. (2009) showed that during the catalytic ozonation of several pharmaceutical compounds no significant adsorption could be observed for any of them, irrespective of pH. Accordingly, Zhao et al. (2009) suggested that the adsorption of nitrobenzene was too small to make a significant contribution to its degradation on cordierite modified catalysts, while a considerable enhancement of the degradation efficiency was achieved in comparison with homogeneous ozonation. This result suggested that the oxidation reactions of organic compounds occur mainly in the aqueous phase, and not on the surface of the catalyst.

In case that the adsorption of organics played a significant role on the mechanism of catalytic ozonation, a difference would be expected between $k_{HO\bullet}^{hc}$ and $k_{HO\bullet}^{h}$, which could be revealed by analysing kinetic data. For this, we performed competitive kinetics analyses for the ozonation of clofibric acid, fenofibric acid and linuron using atrazine as reference compound. The results for clofibric and fenofibric acids are shown in Figure 2, in which solid lines represent the homogeneous relationship according to the following expression:

$$m = \frac{k_{O_3(A)}^{h} + k_{HO\bullet(A)}^{h} R_{ct}^{h}}{k_{O_3(ATZ)}^{h} + k_{HO\bullet(ATZ)}^{h} R_{ct}^{h}} \qquad [7]$$

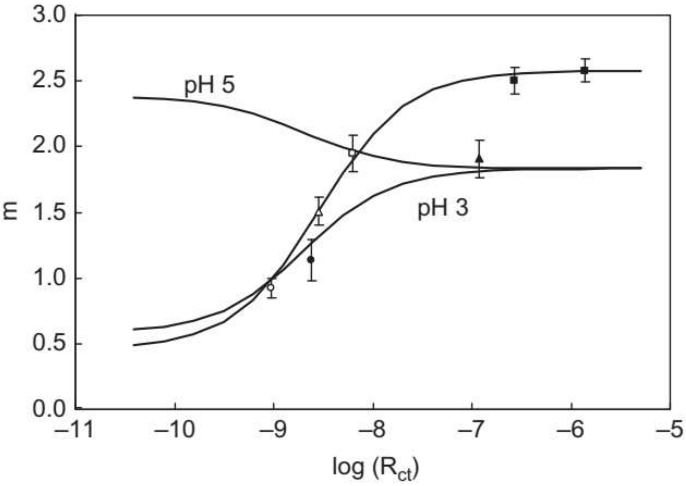

Figure 2. Parameter m defined in Eq. 6 as a function of R_{ct} for the catalytic ozonation of clofibric acid and atrazine in runs performed on TiO_2 (1 g/L) at pH 3 (●) and 5 (▲). Also, for fenofibric acid and atrazine in spiked wastewater for non-catalytic runs (○) and on 1 g/L of Al_2O_3 (Δ) and 1 g/L of MnO_x/Al_2O_3 (□). Filled squares represent initial and final values obtained during the ozonation of fenofibric acid on MnO_x/Al_2O_3 in PBW.

At high (low) values of R_{ct}^{h} the observed hydroxyl-to-ozone ratio equals the ratio of indirect (direct) ozonation rate constants. For the case of clofibric acid the two lines, labelled pH 3 and 5 represent the change observed in $k_{O_3}^{h}$ with pH. It might be expected that the rate constant $k_{HO\bullet}^{hc}$ would differ from those of the homogeneous system, but the points corresponding to catalytic and non-catalytic reactions can be precisely located along the homogeneous theoretical line. This stands true for TiO_2, Al_2O_3, and MnO_x/Al_2O_3 either in spiked wastewater or in PBW. The results from catalytic ozonation in the wastewater matrix, represented as empty symbols, show that there was a significantly lower value of R_{ct} in comparison with PBW, but also revealed that the use of 1 g/L of MnO_x/Al_2O_3 resulted in a hydroxyl-to-ozone ratio one order of magnitude higher than the corresponding to homogeneous non-catalytic process. As the direct ozonation rate constant was not modified by the presence of metal oxides, the discriminating capacity of the ratio *m* is higher in systems with enhanced production of hydroxyl radicals. This corresponds to the filled squares in Fig. 2, which represent the initial and final values of the hydroxyl-to-ozone ratio during a one-hour ozonation of fenofibric acid. The right square represents the first minute of ozonation, while the left corresponds to a sample taken after 6.5 min on stream. It may be argued that if the rate constant is not affected by MnO_x could be due to an inhibition of organics adsorption due to the slats contained in phosphate buffered water or wastewater. The same effect has been observed, however in pure water making it plain that the catalyst did not affect $k_{HO\bullet}$ in any case. It is to be noted that R_{ct} decreased during runs carried out in PBW as well as for those performed in pure water, while it was essentially constant in spiked wastewater or in PBW with high ionic strength. This behaviour was clearly associated to the presence of radical scavengers in the reaction mixture such as bicarbonate, carbonate, phosphate or t-BuOH. Further details are given elsewhere (Guzman-Pérez et al., 2011).

We also found that the direct catalytic ozonation constant did not differ significantly from zero in any case, the reaction with molecular ozone being a non-catalytic process that takes place in homogeneous phase. Fig. 3 shows the results of the ozonation of atrazine and linuron in fixed bed. The upper (lower) dashed line represents an arbitrary 50% increase in $k^{hc}_{HO\bullet}$ of atrazine (linuron) with respect to the non-catalytic reaction. The symbols represent experiments using PBW without bicarbonate and with two different concentrations of $NaHCO_3$ on MnO_x/SBA15. Repeated symbols correspond to runs performed at different liquid flow rates. A similar result was obtained for Al_2O_3 and MnO_x/Al_2O_3 irrespective of the matrix used. Again, the hydroxyl radical-to-ozone ratio was significantly improved by MnO_x in the catalyst and was higher for Al_2O_3 than for SBA-15. The application of competitive kinetics for three compounds on different catalysts and using different matrixes that included a spiked effluent of a WWTP and PBW loaded with different amounts of bicarbonate, showed no evidence any of the catalysts increased the indirect, hydroxyl-mediated, ozonation rate constant with respect to homogeneous ozonation. The possibility of reaction of non-adsorbed organics with oxidized surface sites or surface-adsorbed oxidants is compatible with our results but would probably lead to different exposure to hydroxyl radical for dissimilar compounds depending on their ability to reach the surface. In competitive kinetics, this effect would have the same consequence than a change in the indirect rate constant with respect to homogeneous reaction, something that was not observed in our work. Our results suggest that the mode of action of metal oxide catalysts during ozonation would be an enhanced generation of oxidant species through the catalytic decomposition of ozone with subsequent reaction in the bulk.

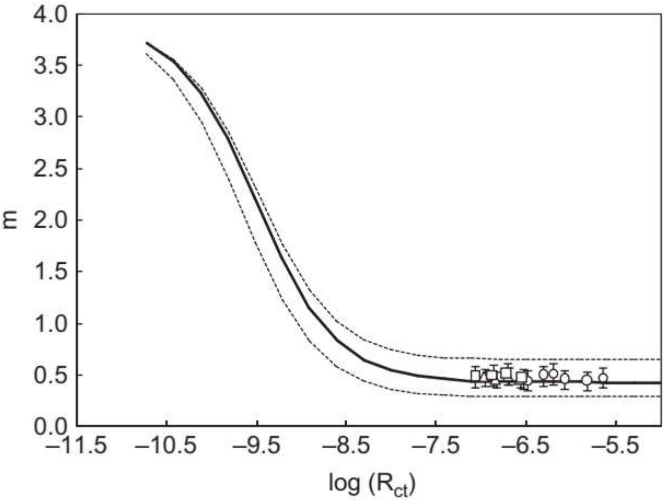

Figure 3. Parameter m defined in Eq. 6 as a function of R_{ct} for the catalytic ozonation of linuron and atrazine in runs performed in fixed bed reactor using MnO_x/SBA15 and PBW (○), $NaHCO_3$ 10^{-3} M (Δ) and $NaHCO_3$ 5 x 10^{-3} M (□).

Metal oxide catalysts improved the efficiency of hydroxyl radical production from ozone with respect to non-catalytic ozonation. The enhancement represented values of R_{ct} near 10^{-6} for MnO_x/Al_2O_3 whereas the maximum value obtained for Al_2O_3 was 3.7×10^{-7} during the ozonation of atrazine and for atrazine conversions <10%. A much higher effect could be appreciated when MnO_x was incorporated into SBA-15, with R_{ct} as high as 4.5×10^{-6} while in similar conditions SBA-15 alone hardly surpassed 10^{-7}. The average increase in R_{ct} was over 30 fold when using MnO_x/SBA-15 with respect to SBA-15 alone, whereas MnO_x/Al_2O_3 increased the efficiency in generation hydroxyl radicals by an average factor of 2.7 with respect to Al_2O_3. For MnO_x/SBA-15, R_{ct} increased threefold with respect to MnO_x/Al_2O_3 under similar conditions. Fig. 4 shows the R_{ct} obtained during the ozonation of atrazine in fixed-bed using SBA-15 and MnO_x/SBA-15 with two different amounts for MnO_x in the bed. The moles of ozone consumed per mole of atrazine decreased for increased amounts of MnO_x, as indicated in the results reported in Fig. 4 which correspond to space time in the 3-7 s range.

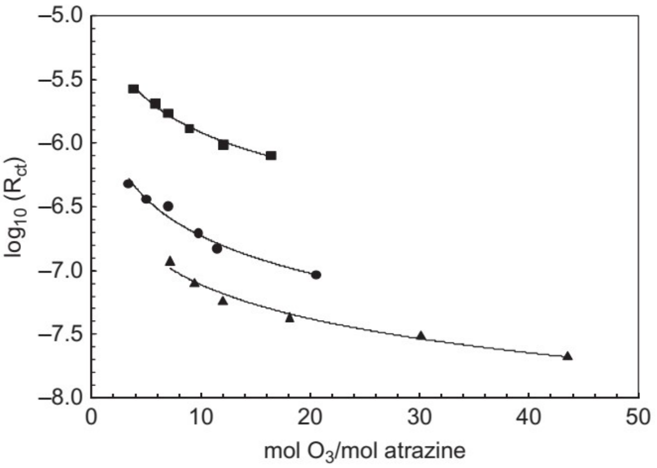

Figure 4. Hydroxyl radical-to-ozone ratio for runs using SBA15 (▲), MnO_x/SBA15, 0.25% MnO_2 (●) and MnO_x/SBA15, 1.0% MnO_2 (■). Weight percentages refer to the whole catalytic bed.

The surface area of MnO_x/Al_2O_3 is one fourth that of MnO_x/SBA-15, that is approximately the ratio a R_{ct} under similar reaction conditions. This suggests a better distribution of the active phase on a larger surface, although the result is also compatible with a higher internal mass transfer resistance in alumina supported catalyst whose particle size (100 μm) is one hundred times higher that of SBA-15 (1.3 μm). The fact that R_{ct} was measured in solution using a neutral non-adsorbing compound is consistent with the assumption that the catalysts promoted the generation of hydroxyl radicals, probably through the formation of surface complexes between ozone and surface hydroxyl groups, but they do not interact significantly with organics.

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Nomenclature

r_A	reaction rate in homogeneous or heterogeneous units, mol L^{-1} s^{-1} or mol kg^{-1} s^{-1}
k_{O_3}	second order rate constant for direct ozonation reaction, L mol^{-1} s^{-1}
$k_{HO\cdot}$	second order rate constant for the reaction with hydroxyl radicals, L mol^{-1} s^{-1}
c_A	concentration of a given organic compound, mol L^{-1}
$c_{HO\cdot}$	concentration of hydroxyl radical, mol L^{-1}
c_{O_3}	concentration of dissolved ozone, mol L^{-1}
K_A	adsorption equilibrium constant, L mol^{-1}
K_{ox}	equilibrium constant for the surface oxidation process, L mol^{-1}
R_{ct}	ratio of $c_{HO\cdot}$ to c_{O_3}, dimensionless
m	parameter defined in Eq. 6, dimensionless

Subscripts and superscripts

o	initial
h	homogeneous reaction
c	catalytic reaction
hc	simultaneous homogeneous and catalytic reaction

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