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Iron type catalysts for the ozonation of oxalic acid in water

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Abstract

Two iron catalysts (Fe(III) and Fe_2O_3/Al_2O_3) have been used in the ozonation of oxalic acid in water at pH 2.5. Percentage removals of oxalic acid were 1.8%, 7% and 30% corresponding to the non-catalytic, homogeneous (Fe(III)) and heterogeneous (Fe_2O_3/Al_2O_3) catalytic ozonations, respectively. Catalytic oxalic acid ozonation leads in all cases to total mineralization. The mechanism of ozonation likely develops through formation of iron-oxalate complexes that further react with ozone without the participation of hydroxyl radicals. Because of the stringent acidic conditions, some metal leaching has been observed and quantified in the heterogeneous process. In the homogeneous catalysis, the kinetics was found to be first order with respect to ozone and oxalic acid while for the heterogeneous catalysis, the kinetic order depends on the concentration of ozone in the gas fed. Thus, at ozone concentrations lower than $30\,\mathrm{mg\,L^{-1}}$, the heterogeneous ozonation is between first and zero order with respect to both ozone and oxalic acid while at higher ozone gas concentrations, the kinetics was found to be first and zero order with respect to oxalic acid and ozone, respectively. This kinetics is supported through an Eley–Rideal mechanism that involves a surface reaction between non-adsorbed ozone and adsorbed oxalic acid. Apparent activation energies of the homogeneous and heterogeneous catalytic ozonations were found to be 18.2 and $13.6\,\mathrm{kcal\,mol^{-1}}$, respectively.

Keywords: Catalytic ozonation; Iron catalysts; Fe(III); Fe_2O_3/Al_2O_3; Water treatment; Oxalic acid

1. Introduction

Chemical oxidation is one of the recommended technologies for the removal of refractory compounds in water treatment. Particularly, advanced oxidation processes (AOPs) or hydroxyl radical-based processes are, a priori, specifically recommended for this purpose. The main drawback of AOPs is, however, the lack of selectivity. Thus, hydroxyl radicals react in water with most of organic compounds at similar rates. Hence, the presence of natural substances such as carbonates, humics, etc, inhibits the oxidation rate of any specific pollutant by trapping hydroxyl radicals. Consequently, appropriate chemical oxidation systems should be more selective towards target compounds.

As recently reported selective oxidation systems can be developed through the use of metal (or metal oxides) catalysts in ozonation processes (Pines and Reckhow, 2002; Beltrán et al., 2003a, b). Catalytic ozonation is an emerging technology, still at research level, that has been the subject of some review works (Legube and Karpel Vel Leitner, 1999; Beltrán, 2003; Kasprzyk-Hordern et al., 2003). This technology is characterized by the use of catalysts to enhance the oxidation of pollutants in water when ozone is applied. Most of the works on this matter mainly focus on the discussion of the variable effects (concentration of ozone, pollutants, catalyst) and on the ozonation rate and comparison with the corresponding

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non-catalytic ozone process (Karpel vel Leitner et al., 2000; Kasprzyk-Hordern and Nawrocki, 2003). Only a few of these works have also dealt with mechanism and kinetics. Thus, two major mechanisms are proposed according to whether or not hydroxyl radicals are formed. For example, previous works report that metals like Co(II), Mn(IV) or Ti(III) form complexes with the organic matter (i.e. oxalic acid) to increase the rate of ozonation (Pines and Reckhow, 2002; Beltrán et al., 2003b, 2004; Ernst et al., 2004; Andreozzi et al., 1992). In other works where activated carbon is used, however, hydroxyl radicals are reported to be formed from the adsorption and surface decomposition of ozone. In these cases, a new AOP is developed (Jans and Hoigné, 1998; Beltrán et al., 2002a).

Among catalysts, iron type catalysts can be recommended because of the abundance of this metal on earth. In fact, iron type catalysts have already been used in ozonation processes to remove different compounds such as phenol, aniline, carboxylic acids, chlorobenzene, chlorophenols, dyes or natural organic matter (Chen et al., 1976; Al-Hayek et al., 1989; Bhat and Gurol, 1995; Cooper and Burch, 1999; Hassan and Hawkyard, 2002; Park et al., 2004).

In this work, Fe(III) catalysts are used both in homogeneous and heterogeneous (as oxide supported on alumina) form to increase the ozonation rate of oxalic acid, one of the products in the ozonation of phenols. The goals of the work is to discuss possible mechanisms of reaction, importance of metal leaching, and contribution of heterogeneous and homogeneous (if any) catalytic ozonations to the overall oxalic acid removal rate.

2. Experimental

$Fe(NO_3)_3 \cdot 9H_2O$ and oxalic acid were purchased from Merck and Aldrich, respectively, and used as received. Ozone was produced from pure oxygen in a laboratory ozonator. γ-Al_2O_3 spherical pellets (Alcoa) were used as supporting material. In some experiments *t*-butanol (Aldrich) was also used to scavenge any possible hydroxyl radical species.

The alumina supported catalyst was prepared by the impregnation method (Cooper and Burch, 1999). The method consisted of adding known amounts of γ-Al_2O_3 to a saturated solution of Fe(III) nitrate and keeping the system agitated for 24 h. Then, after filtration and drying at 105 °C, the impregnated alumina was calcined for 5 h at 800 °C. The manufactured catalyst contained 1.5% Fe and was characterized by N_2 adsorption in a Quantachrome autosorb 1 automated gas adsorption system. The BET specific surface area was found to be $103\,m^2\,g^{-1}$. Porosity and apparent and true densities were determined through a helium and mercury porosimetry with a stereopicnometer and an Autoscan-60 Quantachrome apparatus, respectively. These parameters were determined to be 0.38, 1.26, and $3.53\,g\,cm^{-3}$, respectively. X-ray characterization clearly showed the presence of Fe_2O_3 and Al_2O_3 peaks.

The equilibrium adsorption isotherm for oxalic acid from aqueous solution on the Fe_2O_3/Al_2O_3 catalyst was determined at 20 °C using the batch bottle-point method. Different amounts of catalyst were weighted and suspended into glass bottles containing 50 ml of oxalic acid aqueous solution. The bottles were sealed and placed in an orbital shaker where samples were kept at constant temperature within ±0.1 °C. Equilibrium test duration was 20 days.

Oxalic acid ozonation experiments were carried out in a 1000 mL glass-jacketed vessel provided with an agitation bar. The bar ended in a stainless steel basket ($3 \times 3 \times 3$ cm) at its bottom edge to contain the catalyst (in case of heterogeneous catalysis experiments). Temperature inside the reactor was kept constant by circulating water from a thermostatic batch where the reactor was submerged. The procedure was as follows: 800 mL oxalic acid (and Fe(III), in some cases) aqueous solution of known concentration was first charged and then an oxygen–ozone mixture was continuously bubbled. The reactor was then operated in semibatch mode. No buffer was used to keep the pH that varied less than 0.3 units through the reaction. Reaction time was 3 h.

The same reactor was used for ozone decomposition experiments. Now, ozone saturated aqueous solution with or without catalyst, immediately prepared, was charged to the reactor with no headspace. Then, the reactor was operated batchwise. Samples were withdrawn at regular times. In these experiments, pH 2.5 was maintained with phosphoric acid.

Oxalic acid concentration was determined by liquid chromatography. Details can be found elsewhere (Beltrán et al., 2002b). Ozone in the gas phase was analyzed by means of a GM109 Anseros ozomat analyzer based on the absorption of ozone at 254 nm. Concentration of dissolved ozone was determined by the indigo method (Bader and Hoigné, 1981). Total carbon (TC) dissolved in water was also followed with a DC-190 Dorhmann TOC analyzer, based on carbon dioxide infrared absorption. Since experiments were carried out at pH 2.5 TC values corresponded, in fact, to the remaining dissolved organic carbon (TOC).

3. Results and discussion

3.1. Ozone decomposition experiments

A first series of ozone decomposition experiments was carried out in the presence of the studied catalysts.