

Enhancement of gas–liquid mass transfer during the unsteady-state catalytic decomposition of ozone in water

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Received 23 November 2005; received in revised form 24 February 2006; accepted 27 February 2006

Available online 17 April 2006

Abstract

Unsteady mass transfer and kinetic experiments were conducted in a gas–liquid reactor to study the catalytic and non-catalytic decomposition of ozone in water. In the absence of catalyst, first-order decomposition constants and volumetric mass transfer coefficients were determined at temperatures between 20 °C and 30 °C. Catalytic runs were performed on fumed colloidal TiO₂, which primary particles had an average diameter of 20 nm. The evolution of the concentration of ozone in water after introducing a given amount of catalyst was fitted to a kinetic model that assumed two-stage adsorption–decomposition on the catalytic surface. Runs were performed under slightly acidic conditions allowing the adsorption of ozone molecules on Lewis acid sites. A significant enhancement of mass transfer has been linked to the presence of particles. This effect could be attributed to a physical shuttle mechanism involving the adsorption of ozone on surface adhering particles. For bulk concentrations of catalyst up to 0.65 kg m⁻³, the fraction of interface coverage did not reach saturation. The observed behaviour is consistent with the hydrophilic character of titanium oxide. Reaction constants and activation energies were determined for the two chemical steps describing catalytic ozone decomposition.

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Keywords: Adsorption; Catalysis; Ozonation; Enhancement; Titanium oxide

1. Introduction

Ozone has recently received much attention in water treatment technology due to its high capacity for oxidation and disinfection. Commercial applications focus on iron and manganese oxidation, odour control and disinfection, but a more widespread use is expected [1,2]. Two physicochemical factors determine the concentration of ozone in aqueous systems. First, the low solubility of ozone in water limits the mass transfer driving force of gaseous ozone into water and consequently, typical concentrations of ozone during water treatment range from <0.1 mg L⁻¹ to 1 mg L⁻¹. Second, ozone is unstable in water, being the subject of extensive basic chemical research. It has been shown that ozone decomposes spontaneously during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals [3–5].

Municipal and industrial wastewaters usually contain compounds refractory to the conditions of homogeneous

ozonation processes. Moreover, conventional ozonation applied to degradable organic matter led to carboxylic acids and other oxygenated compounds with low rate of mineralization. Another drawback of homogeneous ozonation processes is that alkaline conditions are required for reactions to proceed at a reasonable rate [3,4]. Advanced oxidation processes are intended to oxidize persistent pollutants or their reaction products by enhancing the concentration of hydroxyl radicals or other strong oxidant species [6]. Among other advanced oxidation processes, catalytic ozonation has received particular attention during the last few years in the search for lower costs and simpler operation [7]. Many authors reported promising results using metal oxides, supported metals or carbon catalysts [8]. As for metal oxides, TiO₂, MnO₂ and Al₂O₃ received major attention [9–12]. The surface of metal oxides contains hydroxyl groups that act as Brønsted acid sites and determine the charge of the surface as a function of pH. In addition to this, metal oxides have Lewis acid sites that, in an aqueous solution, allow water molecules to coordinate on their surface [13]. The adsorption of ozone or dissolved organic molecules on the surface of metal oxide requires the displacement of coordinated water and is strongly dependent on the presence of other bases.

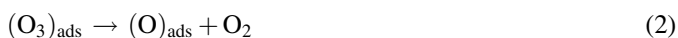
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Nomenclature

C_{O_3}	concentration of ozone (mol m^{-3})
$C_{O_3}^*$	equilibrium concentration of ozone in the liquid phase (mol m^{-3})
C_{OH^-}	concentration of hydroxide ions (mol m^{-3})
c_s	bulk concentration of solids in the liquid phase ($\text{kg}_{\text{solids}} \text{m}^{-3}$)
$c_{s,i}$	concentration of solids in liquid at the gas–liquid interface ($\text{kg}_{\text{solids}} \text{m}_{\text{liquid}}^{-3}$)
c_t	total concentration of active sites (mol kg^{-1})
D_{O_3}	diffusivity of ozone in water ($\text{m}^2 \text{s}^{-1}$)
E	enhancement factor
Ha	first-order Hatta number, $Ha = \sqrt{k_d D_{O_3}} / k_L$
Ha'	Hatta number defined by Eq. (9)
J_{O_3}	mass transfer rate of ozone ($\text{kmol m}^{-2} \text{s}^{-1}$)
$J_{O_3}^p$	mass transfer rate of ozone through the part of the surface covered by particles ($\text{kmol m}^{-2} \text{s}^{-1}$)
K_s	Langmuir-type adhesion constant defined in Eq. (10) ($\text{m}^3 \text{kg}^{-3}$)
K_L	dimensionless mass transfer coefficient defined by Eq. (11)
k, k_i	kinetic constants for heterogeneous reactions ($\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$)
k_d	kinetic constant of ozone self-decomposition ($\text{s}^{-1}, \text{mol}^{1-n} \text{m}^{3n-3} \text{s}^{-1}$)
k_{La}	volumetric mass transfer coefficient in the liquid phase (s^{-1})
m	partition coefficient of the solute between solid and liquid phases, $(\text{kmol m}_{\text{solid}}^{-3}) (\text{kmol m}_{\text{liquid}}^{-3})^{-1}$
<i>Greek letters</i>	
ζ	interface fractional coverage by adhering particles
ζ_s	maximum possible interface fractional coverage
θ	fractional coverage of catalyst surface

In the case that a Lewis site is accessible to ozone, the mechanism for its adsorption–decomposition on a catalytic surface would follow a mechanism similar to that used for explaining gas-phase decomposition [10,14]:



In aqueous solution, the hydroxide ion is expected to act as a strong inhibitor of the adsorption ability of the catalyst by blocking Lewis acid sites. Therefore, the catalytic activity at high pH should proceed by a redox mechanism involving surface hydroxyl groups [12]. Ozone would react with them to yield an ozone anion radical or another active species able

to oxidize organic compounds either in solution or on the surface [10,15].

The presence of fine particles in a gas–liquid reactor enhances gas–liquid mass transfer due to an effect that was first described by Kars et al. [16]. The mechanism involves the physical adsorption of the transferred component from the gas phase and its subsequent desorption to the bulk of the liquid. Hydrophobic particles tend to adhere to the interface and accumulate in the mass transfer zone leading to higher enhancement factors but the effect was also described with relatively hydrophobic particles [17]. In the case of catalytic solids, the enhancement can be due to the increased reaction rate near the interface originated by a greater concentration of catalyst [18].

The aim of this paper is to obtain a kinetic expression for the aqueous decomposition of ozone using fine particles of titanium oxide as catalyst. The influence of temperature over the range of practical interest in ozonation has been studied to determine the activation energies of catalytic and non-catalytic reactions. Catalytic reactions were carried out in unsteady state by adding an aqueous suspension of the catalyst to a stirred bubble reactor operating in semicontinuous mode. Special attention was paid to the influence of the amount of catalyst on the mass transfer rate. The assumption underlying the approach followed in this paper is that under slightly acidic conditions, Lewis acid sites on titanium dioxide may adsorb ozone both dissolved in the liquid and directly from the gas phase. The concentration of ozone in water was then considered the result of the simultaneous mass transfer, physical adsorption and simultaneous homogeneous and catalytic decomposition reactions.

2. Experimental

2.1. Materials, experimental setup and procedure

Titanium dioxide Degussa P25 (80/20 anatase-to-rutile ratio) was used as a catalyst to decompose ozone in double distilled water. The powder has an average particle size of approximately 20 nm and a BET surface of $50 \text{ m}^2 \text{ g}^{-1}$. Ozone decomposition reactions were carried out in a 20 L glass jacketed reactor whose temperature was controlled by a Huber thermostatic regulator. The temperature of the liquid inside the reactor was also monitored throughout the experiment. Ozone was produced by a corona discharge ozonator (Ambiozon, GMF10) that was fed by oxygen from a compressed cylinder supplied by Air Liquide (99.995%).

The mixture of ozone and oxygen was bubbled into the liquid by means of a porous glass disk with a total gas flow that varied from 40 NL h^{-1} to 90 NL h^{-1} . The content of the vessel was agitated with a two-blade impeller operating at velocities of 100–200 rpm. The ozone decomposition experiments were conducted in a semicontinuous mode using a fixed volume of water. Catalytic decomposition runs were performed by introducing the catalyst once the steady state was reached for the reaction in pure water. Experiments were carried out under slightly acidic conditions (pH 5, at which this variable

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