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Adsorbed Phase Ozonation of Water-Dissolved Organic Pollutants Using High-Silica Zeolites

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Abstract. This paper deals with a novel adsorbed phase ozonation process that enhances the reaction rate between ozone and organic pollutants, especially focusing on their reaction kinetics on ZSM-5s. In this study, we elucidated that adsorptive concentrations in ozone and organic chemical were dominant factors for the increases in reaction rate, and developed a novel method for predicting the reaction rates between ozone and organic chemical on ZSM-5s.

Keywords: ozone, adsorption, ZSM-5, reaction, micropore

1. Introduction

Ozonation is a potential method for decomposing organic pollutants, and have been widely used in water treatments. However, slowness of oxidation for some refractory pollutants and harmful by-products are serious problems in the conventional ozonation. Aiming at the simultaneous solution of these problems, a novel ozonation has been proposed through the use of ozone adsorbent (Fujita et al., 2004a). At the first step of our research, we found ZSM-5s adsorb a large amount of ozone from aqueous phase and its adsorption-desorption process was almost reversible. These facts mean ozone dissolved in water was highly concentrated on ZSM-5s (Fujita et al., 2004a). Also, ZSM-5s strongly adsorb organic pollutants. These suggest both ozone and organic pollutants can be highly concentrated by their co-adsorption and concentrating the reactants enhances the reaction rates. In fact, we performed a series of experiments for TCE deomposition under the adsorbed condition and found the reaction rate in the adsorbed phase was much higher than that in bulk water. (Fujita et al., 2004b). However, the detailed reaction mechanisms in the adsorbed phase has not been made clear. Therefore, the present study focuses on the quantitative investigations of the reaction in the adsorbed phase to provide useful data for engineering design of the adsorbed phase ozonation process.

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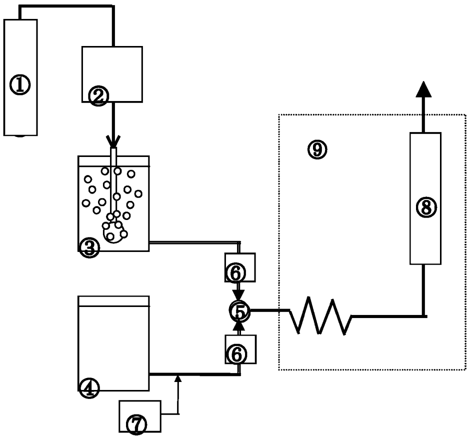

①Oxygen tank ②Ozone generator ③Ozone stock solution ④Distilled water
⑤Mixing vessel ⑥Dual plunger pump without pulsating current
⑦Syringe pump with high concentration of organic chemical solution
⑧Packed column of adsorbents ⑨Constant temperature bath

Figure 1. Schematic diagram of experimental apparatus.

2. Experimental Procedure

2.1. Adsorbents Used and Model Organic Chemical

The adsorbents used were ZSM-5s with different SiO_2/Al_2O_3 ratios (30,80,3000). The SiO_2/Al_2O_3 ratio is a dominant factor for ozone adsorption capacity (Fujita et al.,2004a). The ZSM-5s were supported by the silica-based binder. The ratio of ZSM-5 to binder is 4.0 in weight. Ethanol and acetaldehyde, whose second-order reaction rate constants with ozone were 0.9 and 1.7 M^{-1} s^{-1}, respectively, were selected as the model chemicals to react with ozone.

2.2. Experimental Apparatus

Figure 1 shows the schematic diagram of experimental apparatus. This consists of a part to feed an ozone solution, a part to feed the aqueous solution of oraganic chemical, and a packed column of adsorbents. An constant concentration of ozone solution was prepared in a 1 L glass tank by bubbling gaseous ozone generated by an ozone generator. A constant concentration of the organic chemical solution was prepared by mixing the distilled water and organic chemical solution fed by syringe type micro feeder. The ozone and organic chemical solutions were pumped into a 20 mL mixing vessel from different lines. The mixed solution thus prepared was then introduced into a packed column of adsorbents by a dual plunger pump without pulsating current. Ozone concentrations at the inlet and outlet of the column were measured using indigo method (Bader et al., 1980) after steady state in order to observe the apparent reaction rate between ozone and organic chemical in the column.

3. Kinetic Model

We assumed the reaction took place via four processes: mass transfer in laminar film, mass transfer in macropore, mass transfer in micropore, and reaction in micropore. In this study, we neglected the influence of the mass transfer in micropore on the apparent ozone decay. Furthermore, assuming the reaction in adsorbed phase between ozone and organic chemical is written by the second-order reaction, the reaction kinetic is described by the Eqs. (1)–(4):

$$u\frac{\partial[O_3]}{\partial z} + N_b = 0 \tag{1}$$

$$N_b = K_L a_v([O_3] - [O_3]_s) = -D_{eA} a_v \left(\frac{\partial[O_3]}{\partial r}\right)_{r=R_0} \tag{2}$$

$$D_{eA}\left(\frac{\partial^2[O_3]}{\partial r^2} + \frac{2}{r}\frac{\partial[O_3]}{\partial r}\right) - \varepsilon_p K[M][O_3] = 0 \tag{3}$$

$$w = \rho_s A z \tag{4}$$

Table 1. Experimental conditions and parameters used for the calculation.

	Experimental conditions	Parameters for calculation
u [m/s]	2.1×10^{-3}	2.1×10^{-3}
$\varepsilon[-]$	0.37	0.37
R_0[m]	$(2.5\text{–}3.0) \times 10^{-4}$	2.8×10^{-4}
ρp[kg/m^3]	930	930
ρs[kg/m^3]	580	580
ρ [Pa s]	1000	1000
μ [kg/m^3]	0.01	0.01
V_p [mL/g]^a	1.50×10^{-1}	1.50×10^{-1}
A[m^2]	7.85×10^{-5}	
D_e[m^2/s]^b		1.60×10^{-9}

[a] Mercury porosimetry.

[b] Calculated by the analysis of breakthrough curves.

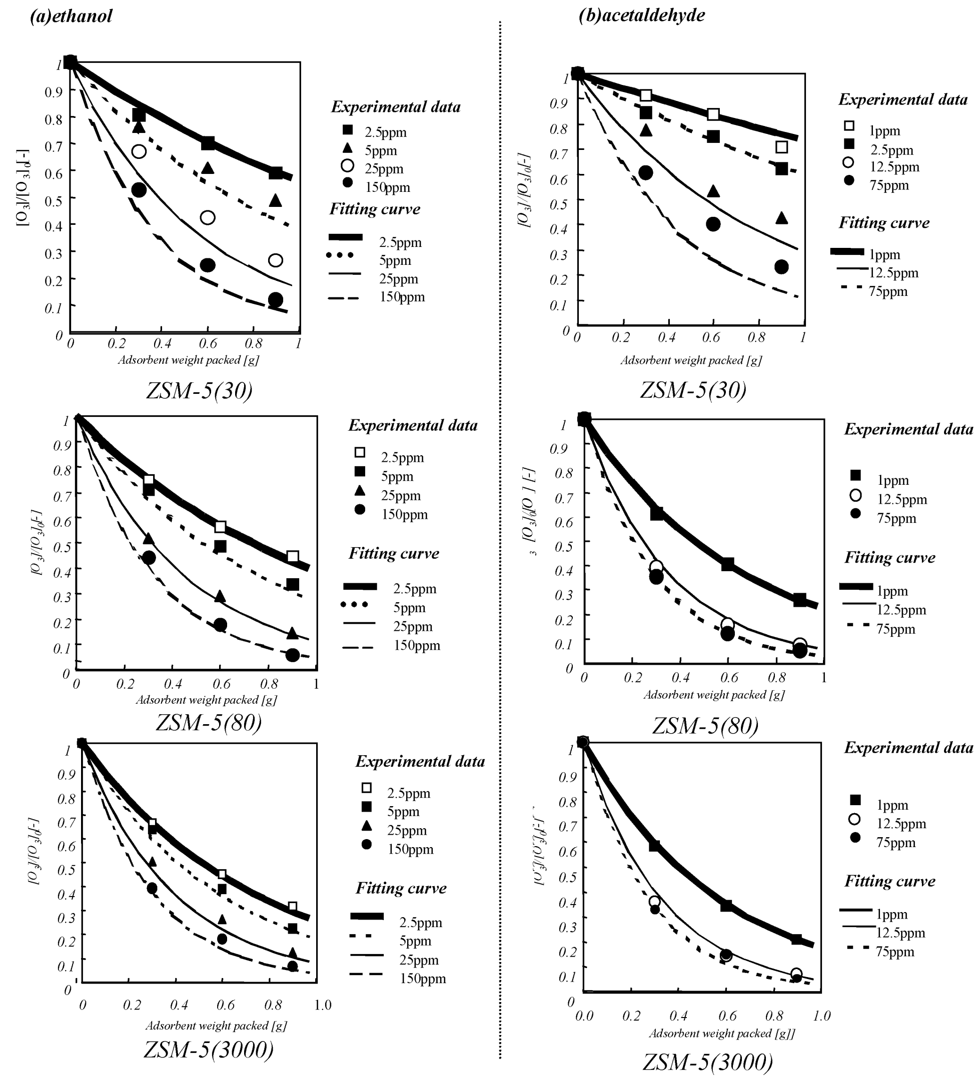

Figure 2. Ozone consumption by ethanol or acetaldehyde in adsorbed phase.

The values of K_L, a_v, ε, and D_{eA} were estimated from Eq. (5) (Carberry et al.,1960), (6)–(8).

$$k_L = 1.15\left(\frac{2R_0 u\rho}{\mu\varepsilon}\right)^{-0.5}\left(\frac{u}{\varepsilon}\right)\left(\frac{\mu}{\rho D_m}\right)^{-\frac{2}{3}} \tag{5}$$

$$a_v = \frac{3\rho_s}{R_0\rho_p} \tag{6}$$

$$\varepsilon = 1 - \frac{\rho_s}{\rho_p} \tag{7}$$

The experimental conditions and the values of parameters for calculations were shown in Table 1.

4. Results and Discussion

4.1. Reaction Rate in Adsorption Phase

Figure 2 shows the ozone decompositions by ethanol or acetaldehyde. The reaction rate constants between ozone and organic chemical per unit micropore volume, K, were calculated by curve-fitting the solution of Eqs. (1)–(4) to the experimental data, as shown in Fig. 2. Resultant K values thus calculated are shown in Table 2. These K values were much larger than the reaction rates in bulk phase.

Table 2. Adsorption characteristics and Reaction rate constants in adsorbed phase.

	β_{O3}	β_M	$K \times 10^4$
ZSM-5 (30)			
Acet aldehyde	0.0244	0.0296	4.42
Ethanol		0.0264	0.883
ZSM-5 (80)			
Acet aldehyde	0.0645	0.0451	31.5
Ethanol		0.0295	4.16
ZSM-5 (3000)			
Acet aldehyde	0.125	0.0253	47.3
Ethanol		0.0190	8.83

4.2. *Interpretation of K Values*

The adsorption equilibria for ethanol and acetaldehyde on ZSM-5s are all linear under our experimental conditions. The adsorption equilibrium for ozone is also linear (Fujita et al., 2003a). Adsorption constants, β_{O3} and β_M are shown in Table 2. Thus, we can assume that the adsorption of ozone and that of the organic chemical are not influenced by each other when they are co-adsorbed on ZSM-5s. Thus, the concentrations of ozone or organic chemical in the pore of ZSM-5s,$[O_3]_{\text{micropore}}$ or $[M]_{\text{micropore}}$ was estimated by the Eqs. (8) and (9), respectively:

$$[O_3]_{\text{micropore}} = \frac{\text{ozone amount adsorbed unit adsorbent weight}}{\text{micropore volume per unit adsorbent weight}} = \frac{\beta_{O3}[O_3]}{V_p} \quad (8)$$

$$[M]_{\text{micropore}} = \frac{\text{organic chemical amount adsorbed per unit adsorbent weight}}{\text{micropore volume per unit adsorbent weight}} = \frac{\beta_M[M]}{V_p} \quad (9)$$

In the Eqs. (8) and (9), we assumed ozone and organic chemicals were all adsorbed in the micropore of ZSM-5s and they were adsorbed "in the micropore space" rather than "on adsorbent surface". Furthermore, when the reaction mechanism in the adsorbed phase is assumed to be the same as that in the bulk phase, the reaction rate can be expressed as Eq. (10), and the reaction rate constant on ZSM-5, K, can be predicted from the Eq. (11).

$$k[O_3]_{\text{micropore}}[M]_{\text{micropore}} = \frac{\beta_{O3}\beta_M}{V_p^2}k[O_3][M] \quad (10)$$

$$K = \frac{\beta_{O3}\beta_M}{V_p^2}k \quad (11)$$

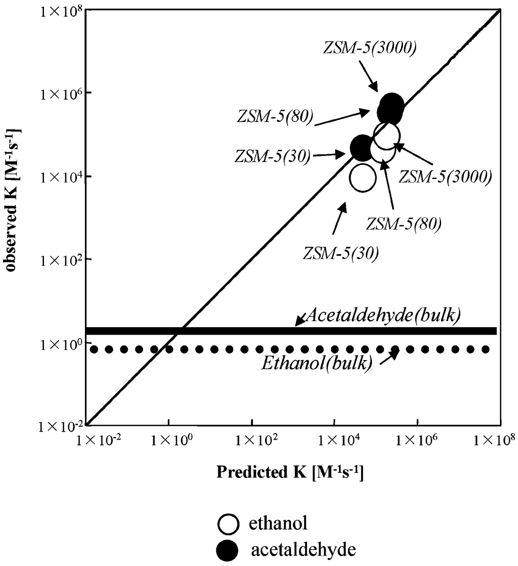

Figure 3. Comparison between the *K* predicted and *K* experimentally derived.

4.3. *Comparison Between K Values Experimentally Derived and those Predicted*

Figure 3 shows the comparison between *K* values experimentally derived and those predicted from the Eq. (11). The experimental *K* values were in good agreement with those predicted, as shown in Fig. 3. This means we can simply design the adsorbed phase ozonation process if the adsorption constants β_{O3} and β_M, adsorbent characteristics, V_p, the direct rate constants in bulk phase, k, and stoichiometric relation between ozone and organic chemical is already known.

5. Conclusion

The reaction behaviors between ozone and organic chemicals on ZSM-5s were successfully described. The reaction rate constant in adsorption phase can be roughly predicted from adsorption constants for ozone and organic chemical adsorptions and the reaction rate constant in aqueous phase, suggesting that the quick reaction on ZSM-5s is primarily due to the adsorptive concentrations of ozone and organic chemical. The proposed process can be roughly and simply designed using the kinetic model proposed in this study.

Nomenclature

a_v	Surface area per unit volume of the packed bed
D_{eA}	Effective diffusion coefficient
k	Reaction rate constant of ozone with a chemical in aqueous phase
K	Reaction rate constant of ozone with a chemical in adsorption phase
K_L	Mass transfer coefficient of ozone in laminar film
$[O_3]$	Ozone concentration
$[O_3]_{\mathrm{micropore}}$	Ozone concentration in micropore
$[O_3]_s$	Ozone concentration at the surface of adsorbent
$[\mathrm{M}]$	Concentration of a model chemical to react with ozone
$[\mathrm{M}]_{\mathrm{micropore}}$	Concentration of a chemical in micropore
N_b	Mass transfer of ozone per unit time from bulk phase to adsorption phase
q_{M}	Amount adsorbed of organic chemical
q_{O3}	Amount adsorbed of ozone
r	Length from the center of adsorbent
R_o	Adsorbent radius
u	Superficial velocity
V_p	Micropore volume per unit weight of adsorbent
z	Column length from the inlet
β_{M}	Adsorption constant for organic chemical adsorption, defined as $q_{\mathrm{M}}/[\mathrm{M}]$
β_{O3}	Adsorption constant for ozone adsorption, defined as $q_{\mathrm{O3}}/[O_3]$
ε	Void fraction in the bed
ε_P	Micropore volume per unit adsorbent volume
ρ	Density of water
ρ_p	Apparent adsorbent density
ρ_s	Packing density of adsorbent
μ	Viscosity of water

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