Influence of Surface Texture and Acid–Base Properties on Ozone Decomposition Catalyzed by Aluminum (Hydroxyl) Oxides

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ABSTRACT

The decomposition of aqueous ozone in the presence of three aluminum (hydroxyl) oxides was studied, respectively. It was hypothesized that surface hydroxyl groups and acid-base properties of aluminum (hydroxyl) oxides play an important role in catalyzed ozone decomposition. The variables investigated were oxide dose, aqueous pH, presence of inorganic anions (sulfate and nitrate), the effect of tert-butyl alcohol (TBA) and surface hydroxyl groups density of the three aluminum (hydroxyl) oxides. All three aluminum (hydroxyl) oxides tested, i.e. γ-AlOOH (HAO), γ-Al_2O_3 (RAO) and α-Al_2O_3 (AAO), enhanced the rate of ozone decomposition. The net surface charge of the aluminum (hydroxyl) oxides favored in catalyzed ozone decomposition. The greatest effect on catalyzed ozone decomposition was observed when the solution pH was close to the point of zero charge of the aluminum (hydroxyl) oxide. Sulfate and nitrate were substituted for the surface hydroxyl groups of the aluminum (hydroxyl) oxides, which then complexed with Al^{3+} in a ligand exchange reaction. Therefore, inorganic anions may be able to inhibit catalyzed ozone decomposition. It was confirmed that surface hydroxyl groups were important for ozone decomposition with aluminum (hydroxyl) oxides as catalysts. TBA inhibited ozone decomposition in the presence of HAO, RAO and AAO. It was also tested whether aluminum (hydroxyl) oxides catalyzed ozone-transformed hydroxyl radicals. The relationship between surface hydroxyl groups and the ratio of hydroxyl radical concentration to ozone concentration (R_{ct}) was investigated quantitatively. Higher density of surface hydroxyl groups of the aluminum oxide tested was favorable for the decay of ozone into

hydroxyl radicals.

Keywords: aluminum (hydroxyl) oxide; acid-base property; point of zero charge; surface hydroxyl group; hydroxyl radical

Abbreviations:

TBA	tert-butyl alcohol
HAO	γ-AlOOH
RAO	γ-Al_2O_3
AAO	α-Al_2O_3
R_{ct}	the ratio of hydroxyl radical concentration to ozone concentration
PZC	point of zero charge
pCBA	p-chlorobenzoic acid
A_{BET}	BET surface area (m^2 g^{-1})
V_{tal}	total pore volume (mL g^{-1})
V_{micro}	micropore pore volume (mL g^{-1})
D_{avg}	average diameter of pore (nm)
$[O_3]$	dissolved ozone concentration (mg L^{-1})
[catalyst]	catalyst dose (mg L^{-1})
k_{O3}	kinetics rate constant of ozone decomposition alone (min^{-1})
k_{cata}	kinetics rate constant of catalyzed ozone decomposition ($(mol\ L)^{-1}\ s^{-1}$)
k_{TBA}	apparent kinetics rate constant of catalyzed ozone decomposition within TBA (min^{-1})

1. Introduction

Ozone is one of the most powerful oxidizing agents available in water treatment [1]. Ozone can react fast with organic pollutants including double bonds, aromatic groups, and amino groups [2, 3]. In order to enhance the efficiency of ozonation, Ma et al. [4, 5] combined the ozone with homogeneous and heterogeneous catalysts, with or without metallic phases. Catalyzed ozonation is a promising technology for the effective removal from drinking water and wastewater of pollutants that are recalcitrant to conventional water treatments [6]. The main advantages of catalyzed ozonation relative to traditional ozonation are enhanced ozone utilization, increased efficiency of pollutant removal and improved organic matter mineralization [7]. Heterogeneous catalytic ozonation, though less studied than the homogeneous process, is more attractive as it provides greater oxidation efficiency, costs less and it is more feasible for practical application. Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds. The heterogeneous catalysts used are usually MnO_2 [8], TiO_2 [9], Al_2O_3 [10, 11], α-FeOOH [12, 13], activated carbon [14- 17], ZnO [18], noble metals [19, 20] and mixed metal oxides [21]. These catalysts were investigated on removal different organic matter in drinking water or wastewater. Different catalytic mechanisms for degradation different organic matter were proposed.

Aluminum oxides have been used in water treatment technology mainly as an ion exchanger for the removal of inorganic anions such as As and F [22]. The utilization

of aluminum oxides as supports for active species, mainly metals and metal oxides, in the catalytic ozonation of several organic compounds was also studied [12]. Alumina was found to be an effective catalyst for the ozonation of 2-chlorophenol and for refractory organic compounds such as oxalic, acetic, salicylic and succinic acids [23, 24]. In recent years, researchers have realized that the efficiency of ozonation catalyzed by aluminum oxides is mainly a result of their ability to transform ozone into ·OH radicals, which are the strongest oxidants in water. Although there is agreement that catalysts enhance aqueous ozone decomposition by allowing the formation of ·OH radicals, the mechanism of catalyzed ozone decomposition and the relationship between catalysts and their abilities to catalyze ozone decomposition are still not well understood.

Due to the special surface characteristics and structure of aluminum oxides, their applications in drinking water and wastewater purification are increasing. When aluminum oxides are introduced into water, they strongly adsorb H_2O molecules. Chemisorption of water onto aluminum oxide surfaces is considered to be a reaction between the Al ion, an electron acceptor (Lewis acid), and the hydroxyl ion, its electron donor (Lewis base). At the same time, acidity and basicity are the two main parameters determining the catalytic properties of aluminum oxides [25].

The objective of the present work was to study systematically the influence of the surface texture and the acid-base properties of aluminum (hydroxyl) oxides in the

133 catalytic decomposition of ozone in aqueous solution. The behavior of various
134 aluminum (hydroxyl) oxides, including γ-AlOOH (HAO), γ-Al_2O_3 (RAO) and
135 α- Al_2O_3 (AAO), in decomposing aqueous ozone was examined. The influence of the
136 main variables affecting the rate of ozone decomposition (i.e. aluminum oxide dose,
137 solution pH, presence of the OH scavenger tert-butyl alcohol, inorganic anions, as
138 well as structure and acid–base properties of the aluminum (hydroxyl) oxides) were
139 evaluated, thus providing insights into the mechanism of ozonation catalyzed by
140 aluminum oxides.
141
142 2. Experimental
143 2.1 Catalysts and chemicals
144 Catalysts were synthesized in our laboratory. The aluminum oxide γ-AlOOH (HAO)
145 was obtained by precipitating aluminum nitrate with ammonia until pH reached 9.0.
146 The suspension was aged at 30 °C for 10-15 days. Then the precipitate was repeatedly
147 rinsed with deionized water until the conductivity of the supernatant remained
148 constant over three consecutive rinses. The precipitate was further dried at 70 °C. The
149 aluminum oxides γ-Al_2O_3 (RAO) and α-Al_2O_3 were obtained by calcining the HAO at
150 450 °C and 1150 °C for 4 h, respectively. The crystalline phases of the catalysts were
151 confirmed by X-ray diffraction (XRD). The HAO, RAO and AAO were ground and
152 particles with diameters between 0.075 mm and 0.3 mm were used in experiments.
153 All chemicals used were of analytical reagent or higher grade.
154

155 2.2 Analysis

156 2.2.1 Surface texture characterization

157 Surface area, pore volume and average pore size of aluminum (hydroxyl) oxides were
158 obtained on a Surface Area and Porosity Analyzer (Micromeritics ASAP 2020, USA).

159

160 2.2.2 PZC and density of surface hydroxyl groups

161 The point of zero charge (PZC) was determined using the mass titration method
162 described elsewhere [26]. The titration reagents were $HClO_4$ and NaOH. The
163 electrolyte used was sodium perchlorate at ionic strengths of 0.005, 0.05 and 0.5
164 mol L^{-1}.

165

166 The density of surface hydroxyl groups was measured by Grignard method, described
167 by Tamura [27]. The surface hydroxyl groups on metal oxides (-OH) react with
168 methyl magnesium iodile (CH_3MgI) to evolve methane according to the following
169 raction (equation. (1)).

170 $$-OH + CH_3MgI \rightarrow -OMgI + CH_4\uparrow \quad (1)$$

171

172 2.2.3 Aqueous ozone and p-Chlorobenzoic acid (pCBA)

173 The aqueous ozone concentration was measured using the indigo method [28]. The
174 purity of the p-Chlorobenzoic acid (pCBA), which was purchased from Sigma USA,
175 was 98%. A stock solution of pCBA (3.19 mmol L^{-1}) was prepared by dissolving it in
176 distilled water. The concentration of pCBA was analyzed by HPLC (LC-10AVP,

177 Shimadzu, Japan) equipped with UV detection. The chromatograph column used was
178 VP–ODS (Shimadzu, Japan). Samples were analyzed using an eluent (containing 0.5
179 percent H_3PO_4 and methanol in the ratio 7:3) at delivered at 1 mL min^{-1} and detected
180 at 234 nm. The injection volume was 100 μL.
181
182 2.2.4 Sulfate and nitrate
183 The concentrations of sulfate and nitrate after the adsorption by aluminum oxides
184 were determined by a Dionex ICS-3000 ion chromatography equipped with an IonPac
185 AS II-HC (Dionex, USA) ion-exchange column and a conductivity detector. The
186 eluent was a solution of KOH (30.0 mmol L^{-1}) at a flow rate of 1.2 mL min^{-1}.
187
188 2.3 Experimental procedures
189 Catalyzed ozone decomposition experiments were carried out in batch mode at
190 ambient temperatures (20 ± 2 °C). The glass reactor was a flat-bottomed flask with a
191 volume of 1 L. Ozone gas was generated from dried oxygen using a laboratory ozone
192 generator (DHX-SS-1G, Harbin Electrochemistry Engineering Ltd. China). After the
193 generator reached a steady state, ozone gas was bubbled into distilled water in the
194 reactor with a silica dispenser for a desired period. The initial aqueous ozone
195 concentration was controlled by changing the electrical current of the ozone generator.
196 Then, the ozone gas was shut off when the desired ozone concentration reached. The
197 initial aqueous ozone concentration was 1.69 ± 0.02 mg L^{-1} for each experiment.
198 Catalysts were quickly introduced into the reactor. The reactor was instantly sealed

199 and the magnetic stirrer was turned on to initiate the catalytic ozone decomposition
200 reaction. Samples were withdrawn at pre-selected reaction times. After the residual
201 ozone was instantly quenched with indigo. The solution pH was adjusted with $HClO_4$
202 and NaOH when experiments were conducted in distilled water.
203
204 Experiments to determine R_{ct}, the ratio of hydroxyl radical concentration to ozone
205 concentration, were carried out in the reactor described above. Ozone was introduced
206 into the reactor as shown above. The stock solution of pCBA and catalysts were
207 quickly introduced into the reactor. The reactor was instantly sealed and the magnetic
208 stirrer was then turned on to initiate the catalytic ozonation experiments. Samples
209 were collected at pre-selected reaction time and the residual ozone was quenched
210 instantly using a sodium sulfite solution (pre-acidified with sulfuric acid to pH 5).
211 Samples were filtered with cellulose acetate filters (0.45 μm) and were transferred to
212 25 mL volumetric flasks.
213
214 3. Results and Discussion
215 3.1 Textural characterization and acid-base properties of aluminum (hydroxyl) oxides
216 Textural characteristics of the aluminum (hydroxyl) oxides used in the ozone
217 decomposition experiments were shown in Table 1. RAO had the largest surface area
218 and pore volume of the three aluminum oxides tested. When the aluminum oxides
219 were calcined at 1150 °C, AAO had the lowest surface area and pore volume. The
220 average particle diameter showed remarkable variation. As the calcination

temperature increased, the particle diameter of the aluminum oxides increased.

Table 2 shows the acid-base properties of the aluminum (hydroxyl) oxides. The PZC and the density of surface hydroxyl groups were determined. The PZC of aluminum (hydroxyl) oxides increased as the calcination temperature increased. For HAO, PZC was within the neutral range. For both RAO and AAO, PZC was within the alkaline range. The density of surface hydroxyl groups decreased as the calcination temperature increased. Under conditions of both high temperature and high pressure, surface hydroxyl groups may dehydrate from the oxide surface. AAO still had some surface hydroxyl groups, for calcined at high temperature but not high pressure.

3.2 First order kinetic model for ozone decomposition and apparent first order kinetic model in the presence of aluminum (hydroxyl) oxides

Aqueous ozone decomposition in distilled water follows first order kinetics expressed by equation (2)

$$-\frac{d[O_3]}{dt} = k_{O_3}[O_3] \quad (2)$$

Aqueous ozone decomposition with catalysts in distilled water follows second order kinetics denoted by equation (3).

$$-\frac{d[O_3]}{dt} = k_{cata}[O_3][catalyst] \quad (3)$$

During the catalyzed ozone decay process, the concentration of solid catalyst did not change. As $k_{O_3-cata} = k_{cata}[catalyst]$, based on apparent first order kinetics, equation (3) can be modified to create equation (4).

$$-\frac{d[O_3]}{dt} = k_{O_3-cata}[O_3] \quad (4)$$

Rate constants for the catalyzed decomposition of ozone can be used to indicate the effectiveness of a catalyst. Using these rate constants, the effect of some major variables can be defined exactly. According to equations (2) and (4), rate constants for ozone decomposition and the apparent rate constant for ozone decomposition with aluminum (hydroxyl) oxides could be obtained from the slope of the relationship between $\ln([O_3]/[O_3]_0)$ and reaction time. Figure 1 shows kinetic plots for ozone decomposition with and without catalysts. The plots show an intial phase of ozone disappearance followed by a phase of slower ozone decomposition. This behavior was also observed for ozone decomposition in natural waters and on activated carbon [3, 29]. In these cases, the first phase, called instantaneous ozone demand (IOD), was explained by the fast consumption of ozone by natural organic matter in natural waters and by the transformation of ozone into activated oxygen groups by activated carbon, which in turn contributes to the overall ozone consumption. The data for the initial phase (approx. 0–10 min) can be fitted to apparent first order kinetics ($R^2 >$ 0.99) (Figure 1). Rate coefficients can be obtained for ozone decomposition with aluminum (hydroxyl) oxides. This coefficient can be considered to describe the amount of ozone uptake by HAO, RAO and AAO. Nevertheless, though the application of the first order kinetic model is not a rigorous method, *k* values obtained from this model were used in this study in order to allow the comparison of the efficiency of the three aluminum (hydroxyl) oxides and to evaluate the influence of several variables on the ozone decomposition rate. Therefore, further discussion will

265 focus mainly on the initial reaction phases.

266

267 A series of ozone decomposition experiments were carried out at constant temperature
268 and solution pH but with varying doses of aluminum (hydroxyl) oxides (0.05–0.4g
269 L^{-1}). In Figure 2 the rate coefficient for ozone decomposition, k_{O_3-cata}, is plotted
270 against the dose of aluminum (hydroxyl) oxides. The ozone decomposition rate was
271 enhanced by an increasing dose of aluminum (hydroxyl) oxides. Over the entire range
272 of doses, the experimental data fit well to a straight line ($R^2 > 0.999$). The slope of the
273 plot was expressed by k_{cata} (Fig. 2).

274

275 Based on these results, ozone decomposition catalyzed by aluminum (hydroxyl)
276 oxides followed second order kinetics with respect to ozone concentration and catalyst
277 dose. Results shown in Figures 1 and 2 confirm the hypothesis of equation (3) and the
278 derivation of equation (4) from equation (3). The observed first order rate constant
279 with respect to ozone concentration for the overall reaction takes into consideration
280 both the heterogeneous reaction taken place on the aluminum (hydroxyl) oxides and
281 the homogeneous reactions taken place in the aqueous phase.

282

283 3.3 Effect of solution pH

284 Solution pH is one of the most important factors in the ozone decomposition process.
285 Hydroxide ions (OH^-) were found to be the initiator of the chain reaction in ozone
286 decomposition [1]. Solution pH reflected the concentration of OH^- in solution. The

rate of ozone decomposition increased with increasing pH, which promoted the formation of OH. Solution pH is also one of the most important factors affecting the surface properties of oxides [25]. The surface charges of the metal oxides achieved proton balance. When the net surface charge was zero, the pH of the solution was PZC. Equation (5) shows the proton balance equation of metal oxides. Under acidic conditions (pH < PZC), the surfaces of metal oxides are electropositive, while under basic conditions (pH > PZC), the surfaces of metal oxides are electronegative.

$$MeOH_2^+ \xleftrightarrow{pK_{a1}^{int}} MeOH + H^+ \xleftrightarrow{pK_{a2}^{int}} MeO^- + H^+ \quad (5)$$

The effect of solution pH on the rate of ozone decomposition was studied by analyzing the ozone decomposition reaction constant. The aim of this investigation was to elucidate the effects of solution pH and of the surface charge of aluminum (hydroxyl) oxides on catalyzed ozone decomposition. In Figure 3, the X-axis denotes the pH, while the Y-axis shows the reaction rate constant of catalyzed ozone decomposition minus the rate of uncatalyzed ozone decomposition ($k_{O3\text{-}cata}$–k_{O3}). The values for ($k_{O3\text{-}cata}$–k_{O3}) in Figure 3 indicate the contribution of the catalysts to ozone decomposition. There was an inflexion in the response curves of each of HAO, RAO and AAO. The inflexions appeared when pH was 7.0, 8.77 and 9.0 for HAO, RAO and AAO, respectively. These inflexions show the maximum impact of the catalysts over the pH range 2–11. That is, when solution pH was 7.0, 8.77 and 9.0, HAO, RAO and AAO had the greatest effect on enhancing ozone decomposition. The PZC for each of the aluminum (hydroxyl) oxides were 7.26, 8.26 and 9.40 (Table 2), that is, close to the inflexion in the response curve of each of the oxides. It was concluded

309 that when solution pH was close to PZC of the aluminum (hydroxyl) oxides, the
310 oxides exhibited maximum effect on ozone decomposition. Therefore, zero charge
311 surfaces of aluminum (hydroxyl) oxides and their surface hydroxyl groups were more
312 active than electropositive or electronegative surfaces in catalyzing ozone
313 decomposition.
314
315 3.4 Effect of the presence of inorganic anions
316 In relation to the effect of pH on catalyzed ozone decomposition in the presence of
317 HAO, RAO and AAO, the activity of aluminum (hydroxyl) oxides in catalyzing ozone
318 decay was relative to the surface acid–base properties of the oxides. Because of the
319 unsaturated state of surface electrons on the aluminum oxides, the surface would
320 adsorb water molecules. This behavior may result in the formation of surface
321 hydroxyl groups [25]. Surface hydroxyl groups play an important role in the
322 acid–base properties of aluminum oxides. It was thought that surface hydroxyl groups
323 made a significant contribution to the ability of aluminum oxides to catalyze ozone
324 decomposition. Nevertheless, some inorganic anions in the aqueous phase can be
325 adsorbed onto surfaces of oxides through ligand exchange with surface hydroxyl
326 groups, as shown in equation (6) [25]. If some inorganic anions inhibited the
327 catalyzed ozone decomposition, the activity of the aluminum oxides would be more
328 likely linked with the surface hydroxyl groups.
329 $$MeOH + L^- \Leftrightarrow MeL + OH^- \quad (6)$$
330 Kim et al. [30] had reported anions adsorption on hydrous oxides. In this paper, we

331 focused on sulfate and nitrate adsorption on aluminum oxides especially. Sulfate and
332 nitrate have different complexation affinities for Al^{3+} on the surface of aluminum
333 (hydroxyl) oxides. Figure 4A and Figure 4B showed adsorption process of sulfate and
334 nitrate on aluminum oxides. Results showed that both sulfate and nitrate could be
335 adsorbed on the surface of aluminum oxides. However, adsorption capacity of
336 aluminum oxides for sulfate and nitrate were different remarkably. For both sulfate
337 and nitrate, the adsorption capacity of HAO was the strongest among three aluminum
338 oxides. The adsorption capacity of AAO was the weakest. For outer sphere adsorption
339 mechanism, sulfate was adsorbed on the surface of aluminum oxide more easily.
340 Oppositely, adsorption capacity of nitrate on all aluminum oxides surface was fainter
341 that that of sulfate adsorbed on the surface of aluminum oxide. According to results
342 show in Figure 4A and Figure 4B, more density of surface hydroxyl groups could
343 enhance adsorption capacity both for sulfate and nitrate adsorption on aluminum
344 oxides. Results showed in Figure 4A and Figure 4B confirmed that inorganic anions
345 were adsorbed on the surface of aluminum oxides by ligand exchange with surface
346 hydroxyl groups. Adsorption of sulfate and nitrate may resulted in decreasing of
347 surface hydroxyl groups. Figure 4A and Figure 4B also showed different initial
348 concentration anions adsorption. Adsorption of low concentration anion was very faint,
349 resulted in that ligand exchange of anions with surface hydroxyl groups was very
350 feebleness.
351
352 Figure 5 shows the impact of sulfate and nitrate on the rate constants of catalyzed

353 ozone decomposition in the presence of HAO, RAO and AAO. Nitrate and sulfate at
354 50 mmol L^{-1} significantly inhibited ozone decomposition catalyzed by HAO, RAO
355 and AAO (Figure 4). Rate constants for ozone decomposition catalyzed by HAO,
356 RAO and AAO were 1.39 min^{-1}, 1.56 min^{-1} and 1.80 min^{-1}, respectively. When
357 nitrate was present at 50 mmol L^{-1}, rate constants for HAO, RAO and AAO were 0.64
358 min^{-1}, 1.36 min^{-1} and 1.73 min^{-1}. At 50 mmol L^{-1} sulfate, rate constants for HAO,
359 RAO and AAO were 0.61 min^{-1}, 1.34 min^{-1} and 1.63 min^{-1}. The effect of inhibition
360 was greatest for HAO and least for AAO. Sulfate had a greater ability than nitrate to
361 inhibit catalyzed ozone decomposition.
362
363 Sulfate and nitrate ions adsorb onto aluminum (hydroxyl) oxides via a complexation
364 reaction expressed in equation (6). Accordingly, the effect of sulfate and nitrate on
365 ozone decomposition catalyzed by the aluminum oxides was related to hydroxyl
366 groups on the surfaces of the catalysts. Surface hydroxyl groups on HAO, RAO and
367 AAO could be exchanged by the anions. Among the three aluminum oxides, HAO
368 possessed the highest density of surface hydroxyl groups but the effect of inhibition
369 by sulfate and nitrate anions was the greatest. For AAO, the opposite relationship was
370 observed. The hypothesis described above can be confirmed. As the affinity of sulfate
371 with surface hydroxyl groups was much stronger than that of nitrate, sulfate showed a
372 greater ability than nitrate to inhibit the ozone decomposition. The relationship
373 between the effectiveness of inhibition and the density of surface hydroxyl groups,
374 and the affinity of sulfate and nitrate for these surface hydroxyl groups, account for

375 the observation that surface hydroxyl groups on aluminum (hydroxyl) oxides play an
376 important role in catalytic ozone decomposition.
377
378 3.5 Effect of the presence of the ·OH-scavenger tert-butyl alcohol (TBA)
379 In recent years, many researchers considered that enhanced ozone transformation
380 into ·OH radicals occurred when ozone was decomposed in the presence of solid
381 catalysts. To determine whether ozone was transformed into ·OH radicals, tert-butyl
382 alcohol (TBA) was used as an effective scavenger as it does not react with ozone but
383 it does react with ·OH radicals (the second reaction rate constant of TBA with ·OH
384 radicals is 5.9×10^{8} $(mol\ L)^{-1}\ s^{-1}$) [31]. Some inert compounds that have the potential
385 to terminate the chain reaction of ozone decomposition may be formed when TBA
386 reacts with ·OH radicals. At the same time, TBA can not be adsorbed on the surface of
387 metal oxides, for physical-chemical property of TBA. To investigate whether ozone
388 would be transformed into ·OH or not, further ozone decomposition experiments with
389 HAO, RAO and AAO were carried out in the presence of 0.675 mmol L^{-1} TBA.
390 Figure 5 shows the apparent first order rate coefficients obtained from this series of
391 experiments. The rate coefficient decreased significantly compared with that obtained
392 in the corresponding experiment in the absence of TBA, regardless of the aluminum
393 (hydroxyl) oxide present (Figure 6). Results indicated that HAO, RAO and AAO
394 enhanced ozone decomposition primarily through the acceleration of the OH-radical
395 chain reaction in the liquid phase.
396

From the experiments on ozone decomposition using HAO, RAO and AAO in the presence of TBA, the apparent first order kinetic constants k_{cata} and $k_{cata+TBA}$ were calculated. The constant ($k_{cata} - k_{cata+TBA}$) denotes the inhibition effect of TBA on ozone decomposition in the presence of HAO, RAO and AAO. For HAO, RAO and AAO, ($k_{cata} - k_{cata+TBA}$) was 1.305, 1.191 and 1.083 min^{-1}, respectively. The density of surface hydroxyl groups on each of the aluminum oxides was 8.83×10^{-5}, 3.17×10^{-5} and 0.27×10^{-5} $mol\cdot m^{-2}$ (Table 2). This indicates that the inhibition effect of TBA on aluminum (hydroxyl) oxides was enhanced as the density of surface hydroxyl groups increased. Therefore, surface hydroxyl groups account for enhanced ozone decomposition in the presence of aluminum (hydroxyl) oxides.

3.6 Relationship between surface hydroxyl groups and catalytic activity of producing hydroxyl radicals

From the above discussion, aluminum (hydroxyl) oxides exhibit greatest catalytic activity when solution pH is close to PZC of the aluminum (hydroxyl) oxides. It was also shown by experiments testing the effect of sulfate and nitrate that surface hydroxyl groups played an important role in catalytic ozone decomposition in the presence of HAO, RAO and AAO. Based on experiments testing of the effect of TBA, it was confirmed that, during ozone decomposition, ozone was more effectively transformed into OH radicals in the presence of HAO, RAO and AAO than when no catalyst is present. Therefore, density of surface hydroxyl groups of aluminum (hydroxyl) oxides may also be important in catalytic ozone decomposition. Further

experiments were carried out to investigate the relationship between density of surface hydroxyl groups of aluminum (hydroxyl) oxides and the concentration of ·OH radicals transformed from ozone. The R_{ct} value expresses the ratio of ·OH radical concentration to ozone concentration in ozonated water samples (see equations (7) and (8)) [32]. The R_{ct} value is constant during ozonation in any given type of water sample at any given ozone concentration. Here, the R_{ct} value was assumed to be constant for both non-catalytic and catalytic ozonation. This investigation used p-chlorobenzoic acid (pCBA) as a probe compound to determine the R_{ct} value both in non-catalytic and catalytic ozonation. The reaction rate constants of pCBA reacting with ozone and ·OH are $k_{O3/pCBA} \leq 0.15$ (mol L)$^{-1}$ s^{-1} [33] and $k_{\cdot OH/\,pCBA} = 5\times10^{9}$ (mol L)$^{-1}$ s^{-1} [34], respectively. The experiment results showed that only less than 5% of pCBA was adsorbed on aluminum oxides. Therefore, in the oxidation process, pCBA could react with ·OH quickly. Using equations (7) and (8), the R_{ct} value, shown in Table 3, can be obtained for both non-catalytic and catalytic ozonation.

$$R_{ct} = \frac{\int_{t}^{0} [\cdot OH]dt}{\int_{t}^{0} [O_3]dt} \tag{7}$$

$$\ln\left\{\frac{[pCBA]_t}{[pCBA]_0}\right\} = -k_{\bullet OH/\,pCBA}\int_0^t [\bullet OH]\,dt = -k_{\bullet OH/\,pCBA} R_{ct}\int_0^t [O_3]\,dt \tag{8}$$

The R_{ct} values in the presence of HAO, RAO and AAO were much higher than those found for ozonation without a catalyst. This means that aluminum (hydroxyl) oxides were able to transform ozone into OH radicals. The R_{ct} values increased as the density

of surface hydroxyl groups on the aluminum (hydroxyl) oxides increased. These surface hydroxyl groups on the aluminum (hydroxyl) oxides were active in enhancing the generation of hydroxyl radicals from aqueous ozone.

4. Conclusions

The results of this investigation provided evidence of the positive effect of aluminum (hydroxyl) oxides on ozone transformation into ·OH radicals. This effect depended mainly on the dose of aluminum (hydroxyl) oxides, solution pH, inorganic anions and the presence of tert-butyl alcohol. First order kinetics fitted perfectly to the ozone decomposition reaction in the presence of HAO, RAO and AAO. The surface acid–base properties of aluminum (hydroxyl) oxide played an important role in the catalyzed ozone decomposition. The greatest catalytic effect on ozone decomposition was observed when solution pH was close to PZC of the aluminum (hydroxyl) oxide. The net surface charge of the aluminum (hydroxyl) oxide was favorable for catalyzed ozone decomposition. The negative effect of inorganic anions on catalyzed ozone decomposition indicated that surface hydroxyl groups of the aluminum (hydroxyl) oxides contributed to ozone decomposition. The presence of tert-butyl alcohol inhibited ozone decomposition catalyzed by aluminum (hydroxyl) oxide. This indicated that ozone was transformed into hydroxyl radicals during catalyzed ozone decomposition. By investigating the relationship between R_{ct} and the density of surface hydroxyl groups on the aluminum (hydroxyl) oxide, it was confirmed that the greater the density of surface groups the greater was the ability of the aluminum

(hydroxyl) oxide to transform ozone into hydroxyl radicals. Therefore, the surface hydroxyl groups and acid–base properties of aluminum (hydroxyl) oxide play an important role in catalyzed ozone decomposition.

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Figure Caption

528

529 Figure 1. Apparent first order kinetics plots for aqueous ozone decomposition.
530 Experimental conditions were: pH = 5.56; T=20 ± 1 °C; $[O_3]_0$ = 1.69 ± 0.02 mg L^{-1};
531 catalyst dose (if applied): 0.2 g L^{-1}

532

533 Figure 2. Effects of catalyst dose on the apparent rate coefficient of ozone
534 decomposition. Experimental conditions were: pH = 5.56; T = 20 ± 1 °C;
535 $[O_3]_0$ = 1.69 ± 0.02 mg L^{-1};

536

537 Figure 3. Changes in the reaction rate constant with aluminum (hydroxyl) oxides
538 minus the reaction rate constant without aluminum (hydroxyl) oxides at different pH
539 values. Experimental conditions were: T = 20 ± 1 °C; $[O_3]_0$ = 1.69 ± 0.02 mg L^{-1};
540 catalyst dose = 0.2 g L^{-1}

541

542 Figure 4A. Adsorption of sulfate on the surface of aluminum oxides. Experimental
543 conditions were : T = 20 ± 1 °C; catalyst dose = 0.2 g L^{-1}; pH = PZC of aluminum
544 oxides (7.26, 8.26 and 9.40 for HAO, RAO and AAO, respectively)

545

546 Figure 4B. Adsorption of nitrate on the surface of aluminum oxides. Experimental
547 conditions were : T = 20 ± 1 °C; catalyst dose = 0.2 g L^{-1}; pH = PZC of aluminum
548 oxides (7.26, 8.26 and 9.40 for HAO, RAO and AAO, respectively)

549

Figure 5. Effects of inorganic anions on the apparent rate coefficient of ozone decomposition. Experimental conditions were: T = 20 ± 1 °C; $[O_3]_0$ = 1.69 ± 0.02 mg L^{-1}; $[NO_3^-]_0$ = $[SO_4^{2-}]_0$= 50 mmol L^{-1}; catalyst dose = 0.2 g L^{-1}; pH = PZC of aluminum oxides (7.26, 8.26 and 9.40 for HAO, RAO and AAO, respectively)

Figure 6. Effects of the presence and absence of TBA on the apparent rate coefficient of ozone decomposition. Conditions of experiments: T = 20 ± 1 °C; $[O_3]_0$ = 1.69 ± 0.02 mg L^{-1}; $[TBA]_0$ = 0.675 mmol L^{-1}; catalyst dose = 0.2 g L^{-1}; pH = PZC of aluminum oxides (7.26, 8.26 and 9.40 for HAO, RAO and AAO respectively).