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Mechanism of heterogeneous catalytic ozonation of p-chloronitrobenzene in aqueous solution with iron silicate dried at different temperatures

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ABSTRACT

The degradation efficiencies of p-chloronitrobenzene (pCNB) in aqueous solution by processes employing ozone alone and ozone/iron silicates based on iron silicates dried at 60, 250, 600, or 800˚C were investigated. The results demonstrated that iron silicate dried at 60˚C possessed better catalytic capacity for the ozonation of pCNB than that dried at higher temperatures owing to increased concentrations of hydrogen peroxide (H_2O_2) and the formation of hydroxyl radicals (·OH). Adsorption of pCNB on the surface of iron silicate exhibited no remarkable influence on the degradation efficiency of pCNB. An increase in the drying temperature was found to slightly increase the adsorption ability and significantly reduce the catalytic activity of the iron silicate. Because of the formation of a new crystalline phase, the catalytic activity of iron silicate dried at 800˚C was the lowest. The results of the mechanism analysis suggest that Fe_2O_3, FeOOH, and silicato-iron(III) surface complexes are the dominant components of catalytic activity in the iron silicate catalytic ozonation of pCNB. Moreover, the surface hydroxyl groups of the iron silicate determine the initiation of ·OH from ozone decomposition.

Keywords: Catalytic ozonation; PCNB; Iron silicate; Hydroxyl groups

1. Introduction

Through its primary use as a raw materials, such as pesticide, herbicide, dyestuffs, medicine, antioxidant and so on, p-chloronitrobenzene (pCNB) has become widely dispersed in water and soil [1]. Previous experiments [2] on animals and humans have indicated that pCNB can damage the liver and spleen, may cause a number of diseases such as high-iron-hemoglobin and anemia, and is also implicated in gene mutation. Therefore, the remediation of pCNB in aqueous solutions is of significant environmental concern. In the field of water treatment, heterogeneous catalytic ozonation has gained increasing attention due to its potentially high effectiveness in the degradation of refractory organic pollutants, and its relatively low negative effect on water quality [3–7]. In recent years, several researchers have reported the degradation of pCNB in aqueous solution by heterogeneous catalytic ozonation processes. The experimental results indicate that, relative to processes involving ozone alone, the

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removal efficiency of pCNB is significantly promoted in the presence of heterogeneous catalysts, such as FeOOH [8], manganese silicate [9], and pumice [10]. Moreover, the degradation of pCNB has been found to follow the hydroxyl radical (·OH) oxidation mechanism in these processes. However, the initiation and formation mechanism of ·OH are not clearly understood in heterogeneous catalytic ozonation processes because any given catalyst is only active under particular conditions and responds only to particular groups of organic compounds to be oxidized [11].

Iron silicate is a chemically and thermally stable mineral material that has been used in many applications [12,13], such as in water treatment as a coagulant [14], and in the field of catalysis [15]. The high density of surface hydroxyl groups (–OH) and active elements make iron silicate a good catalyst for enhancing the ozonation process [16]. However, the reaction mechanism of iron silicate-catalyzed ozonation is not clear.

The objective of this study is to clearly reveal the reaction mechanism of the iron silicate catalytic ozonation process by means of the following activities involving iron silicate dried at different temperatures. (1) Investigate the effect of the drying temperature of iron silicate on its catalytic activity for the degradation of pCNB in the ozonation process. (2) Investigate the effect of the drying temperature on the generation of hydrogen peroxide (H_2O_2) and ·OH in the iron silicate catalytic ozonation process. (3) Elucidate preliminarily the effect of the composition and surface characteristics of iron silicate dried at different temperatures on their catalytic ozonation of pCNB in aqueous solution.

2. Materials and methods

2.1. Materials

We purchased pCNB (99.5% purity) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO; >97%) from USA Chem service. HPLC-grade methanol was obtained from Sigma Aldrich (USA). Sodium silicate ($Na_2SiO_3{\cdot}9H_2O$), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), sodium thiosulfate (Na_2SO_3), hydrochloric acid (HCl), sodium hydroxide (NaOH), and indigo were all of analytical grade, and used without further purification. The stock solution of pCNB was prepared at 100 mg L^{-1} by dissolving 100 mg pCNB into 1,000 mL of ultra-pure water (18 MΩ cm). All glassware equipment used in the experiments were soaked in a solution of H_2SO_4–$K_2Cr_2O_7$ overnight, and then washed with tap water followed by washing with distilled water three times.

The catalysts were synthesized in the laboratory. Iron silicate was obtained by chemical coprecipitation of iron nitrate with aqueous sodium silicate, until the mixture attained a pH of 9.0. The suspension was incubated at 40℃ for 24 h. The precipitate was then repeatedly rinsed with ultra-pure water until the conductivity and pH of the supernatant remained constant. The precipitate was dried at 60℃ for 12 h, and the tawny powder iron silicate (60℃) was obtained. The other iron silicate catalysts (250, 600, and 800℃) were prepared by further drying iron silicate (60℃) samples at 250, 600, and 800℃ for 4 h, respectively. The iron silicate powders were ground, and the resulting particles with diameters ranging from 0.075 to 0.3 mm were employed.

For comparison of the catalysis activity, we also synthesized silicon dioxide (SiO_2), iron oxide (Fe_2O_3), silicon hydroxide ($Si(OH)_4$), and iron hydroxide (FeOOH) according to the literature [17–19].

2.2. Ozonation experiments

The experiments of pCNB removal from an aqueous solution were conducted in a 1.2 L reactor in the bath mode at room temperature (20 ± 1℃). For the purpose of comparison, ozonation experiments both with iron silicate dried at one of the four temperatures discussed above and without iron silicate (i.e. with ozone alone) were performed in the same system under identical experimental conditions. For each experiment, 1 L deionized water with the pH pre-adjusted by NaOH or HNO_3 was first transferred into the reactor. Then, ozone gas produced from pure oxygen (Harbin Gas Co., Ltd, 99.999%, China) through a CF-G-3–010 g ozone generator (Qingdao Guolin Industry Co., Ltd, China) was continuously injected into the aqueous solution and dispersed by means of a silica bubble diffuser until the desired concentration is attained. The desired amounts of catalyst and pCNB stock solution were immediately dosed into the reactor. The reactor was quickly sealed and agitated by a magnetic stirrer. Samples were obtained after reaction for 0, 1, 3, 5, 10, and 15 min and quenched by sodium sulfite solution (0.1 mol L^{-1}). The quenched samples were analyzed to determine the pCNB concentration using the method described below. All experiments were conducted in triplicate.

2.3. Analytical methods

The dissolved ozone concentration in aqueous solution was measured by the indigo method [20]. The concentration of pCNB was determined using an Agilent 1200 high-performance liquid chromatography (HPLC; Agilent, USA) system equipped with an ultraviolet-visible (UV–vis) detector. A reversed-phase

4.6 mm × 250 mm C18 water column was used at room temperature. Elution was conducted by pumping methanol and water (8:2 v/v) at a flow rate of 1.0 mL min^{-1}.

The Brunauer–Emmett–Teller (BET) specific surface area of the samples was measured on an ASAP 2020 physisorption analyzer (Micromeritics Instrument Corp., USA). The density of surface hydroxyl groups was measured according to a saturated deprotonation method described by Laiti and Öhman [21]. X-ray diffraction (XRD) analysis conducted on a Bruker D8 Advance diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å) was used to analyze the crystalline structures of the samples. The chemical composition of the products was measured by X-ray fluorescence spectrometry (XRF) on an Axios PW4400 instrument from He Lanpa sodium Branch Company. The surface charge was measured by a Zetasizer Nano Z zeta potential analyzer (Malevern Instruments, Ltd, UK).

3. Results and discussion

3.1. Characterization of iron silicate dried at different temperatures

The textural characteristics and acid–base properties of the iron silicate used in the catalytic ozonation of pCNB experiments are listed in Table 1. As shown in the table, for the evaporation of the interlayer water in the iron silicate, iron silicate (250℃) had the largest surface area followed by iron silicate (60℃). The pH_{zpc} of iron silicate (60℃) was within the neutral range. The iron silicate dried at temperatures of 250, 600, and 800℃ were within the alkaline range. Conditions of high temperature promote the dehydroxylating reaction of hydroxyl groups from the oxide surface. Therefore, the density of surface hydroxyl groups is observed to decrease with increasing drying temperature.

3.2. Degradation efficiencies of pCNB for the systems considered

The results of both non-catalytic ozonation and catalytic ozonation in the presence of catalysts dried at different temperatures are shown in Fig. 1. The degradation efficiencies of pCNB in the presence of iron silicate were greater than the case where the catalyst was absent, and a remarkable oxidation rate is observed when combining ozone and iron silicate (60℃). As shown in Fig. 1, the degradation efficiency of pCNB in the strictly ozone system attained a value of about 58% after 15 min, and the reduction of pCNB due to adsorption on iron silicate (60℃), iron silicate (250℃), iron silicate (600℃), and iron silicate (800℃) resulted in losses of 2, 3, 3, and 5%, respectively. Comparing the curve for the O_3/iron silicate (60℃) system (a) with the cumulative effect of ozone alone and adsorption on iron silicate (60℃) (e) and (i), an increment of pCNB degradation of approximately 40% was observed. The O_3/iron silicate (250℃) system (b) results in about 97% pCNB conversion after 15 min, indicating an increment of 37% pCNB degradation compared with the cumulative effect of ozone alone and adsorption on iron silicate (250℃) (e) and (h). The O_3/iron silicate (600℃) system (c) leads to about 93% pCNB conversion after 15 min, indicating an increment of 30% pCNB degradation compared with the cumulative effect of ozone alone and adsorption on iron silicate (600℃) (e) and (g). The O_3/iron silicate (800℃) system (d) results in about 67% pCNB conversion after 15 min, which provides an increment of 5% pCNB degradation compared with the cumulative effect of ozone alone and adsorption on iron silicate (800℃) (e) and (f). From the above analysis, it can be deduced that: (1) the presence of iron silicate has a significant impact on the ozone for the degradation of pCNB; (2) some active species may be produced during the catalytic ozonation process; (3) pCNB adsorbs little on the surface of the four catalysts, and increasing the catalyst drying temperature increases the adsorption of pCNB on the catalyst surface; (4) the catalytic activity of iron silicate decreased with increasing drying temperature.

3.3. The concentration of H_2O_2 in the systems considered

Ozone in aqueous solution decomposes through the following chain reactions [22]:

Table 1
Surface area, pore diameter, surface hydroxyl groups, and pH_{zpc} values of iron silicate dried at different temperatures

Drying temperature (℃)	BET surface area ($m^2\ g^{-1}$)	Average pore diameter (nm)	Density of surface hydroxyl groups ($mol\ g^{-1}$)	pH_{zpc}
60	339.096	4.6	2.01×10^{-2}	7.04
250	342.03	4.3	1.04×10^{-2}	7.73
600	338.08	5.6	0.31×10^{-2}	8.21
800	76.32	12.1	0.01×10^{-2}	8.64

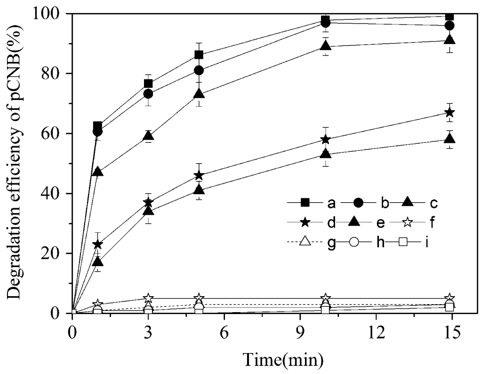

Fig. 1. Degradation of pCNB as a function of reaction time: (a) O_3/iron silicate (60℃); (b) O_3/iron silicate (250℃); (c) O_3/iron silicate (600℃); (d) O_3/iron silicate (800℃); (e) O_3 alone; (f) iron silicate (800℃) adsorption; (g) iron silicate (600℃) adsorption; (h) iron silicate (250℃) adsorption; and (i) iron silicate (60℃) adsorption. Experimental conditions: $[\text{pCNB}]_0 = 100\ \mu\text{g L}^{-1}$; $[O_3]_0 = 0.6\ \text{mg L}^{-1}$; [iron silicate] = $100\ \text{mg L}^{-1}$; solution pH 7.0; reaction time = 15 min; $T = 298$ K.

$$O_3 + HO^- \rightarrow HO_2^- + O_2 \tag{1}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{2}$$

$$2O_3 + H_2O_2 \rightarrow {}^{\cdot}OH + O_2 \tag{3}$$

$$O_3 + HO_2^- \rightarrow {}^{\cdot}OH + O_2^{\cdot -} + O_2 \tag{4}$$

$$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2 \tag{5}$$

$$O_3^{\cdot -} + H^+ \rightarrow {}^{\cdot}OH + O_2 \tag{6}$$

$$O_3 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + O_2 \tag{7}$$

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O \tag{8}$$

$$HO_2^- + {}^{\cdot}OH \rightarrow O_2^{\cdot -} + H_2O \tag{9}$$

To confirm the new species generated from ozone decomposition, the accumulation of H_2O_2 in aqueous solution was investigated for the five systems discussed in Section 2.2. The results are shown in Fig. 2.

As described in Fig. 2, H_2O_2 was formed in the ozone alone, O_3/iron silicate (60℃), O_3/iron silicate (250℃), O_3/iron silicate (600℃), and O_3/iron silicate (800℃) systems due to the decomposition of ozone, and the concentrations of H_2O_2 with the addition of iron silicate were greater than in the case of ozone alone. Moreover, the concentration of H_2O_2 was greatest in the O_3/iron silicate (60℃) system, and increased continuously to $73.22\ \mu\text{g L}^{-1}$ with increasing reaction time up to 15 min. However, increasing the drying temperature of iron silicate progressively reduces the formation of H_2O_2. In the O_3/iron silicate (250℃), O_3/iron silicate (600℃), and O_3/iron silicate (800℃) systems, the H_2O_2 concentrations obtained after 15 min decreased from 69.24 to $18.93\ \mu\text{g L}^{-1}$.

3.4. The detection of ·OH by EPR spectra in the systems considered

As is known, ·OH is another significant species generated from ozone decomposition that attacks organic molecules with rate constants typically in the order of 10^6–$10^9\ \text{M}^{-1}\ \text{s}^{-1}$ [23]. It is therefore necessary to identify directly whether ·OH is generated in the catalytic ozonation processes discussed above. To evaluate the generation of ·OH in the catalytic ozonation processes, the electron paramagnetic resonance (EPR) spectra of DMPO-·OH in these four oxidation processes were obtained in aqueous solution using an EPR spin-trapping technique with a DMPO spin trap. As depicted in Fig. 3, typical EPR spectra are observed for the four processes at the initial DMPO concentration of $100\ \text{mmol L}^{-1}$. An individual EPR spectrum was characterized with quartet lines having a peak height ratio of 1:2:2:1 and the hyperfine splitting constants were aN = aH = 1.49 mT and $g = 2.0059$, which are representative of hydroxyl radicals added to DMPO (i.e. DMPO-·OH) [24]. The experimental evidence indicates that the formation of ·OH was initiated in the four systems considered, and that the relative intensity of DMPO-·OH in these four systems followed the order O_3/iron silicate (60℃) > O_3/iron silicate (250℃) > O_3/iron silicate (600℃) > O_3/iron silicate (800℃). That is to say, the presence of iron

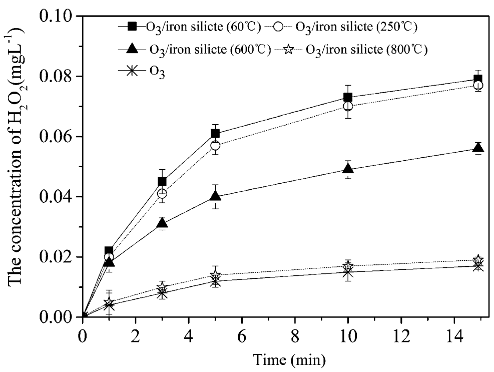

Fig. 2. The concentrations of H_2O_2 in the systems considered. Experimental conditions: $[\text{pCNB}]_0 = 100\ \mu\text{g L}^{-1}$; $[O_3]_0 = 0.6\ \text{mg L}^{-1}$; [iron silicate] = $100\ \text{mg L}^{-1}$; solution pH 7.0; reaction time = 15 min; $T = 298$ K.

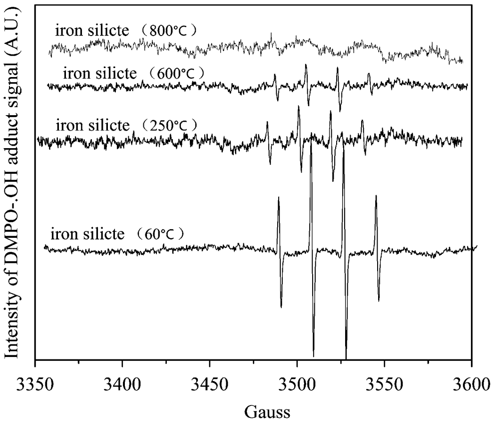

Fig. 3. The EPR spectra of DMPO-·OH for the different ozonation systems in the presence of the DMPO spin trapping agent. Experimental conditions: $[\mathrm{DMNPO}]_0 = 100$ mmol L^{-1}; $[\text{iron silicate}]_0 = 100$ mg L^{-1}.

silicate accelerated the generation of ·OH in the ozonation system. Moreover, the results of Fig. 3 also suggest that high drying temperatures for iron silicate have a negative impact on catalytic ozone decomposition. This result is consistent with the results of H_2O_2 formation.

3.5. The effect of pH on catalytic ozonation

Because of the unsaturation of electrons, water molecules are easily adsorbed on the surface of a metal oxide, which results in the formation of surface hydroxyl groups. From the perspective of heterogeneous catalytic ozonation, the surface hydroxyl groups are very advantageous for catalytic ozonation or catalytic ozone decomposition. As a predominant factor, the pH of a solution has a significant impact on the hydroxyl groups of metal oxides, depending upon the $\mathrm{pH_{zpc}}$ of the catalyst, as shown in the following equations:

$$\mathrm{S-OH+H^+} \overset{\mathrm{pH<pH_{zpc}}}{\longleftrightarrow} \mathrm{S-OH_2^+} \tag{10}$$

$$\mathrm{S-OH+H^+} \overset{\mathrm{pH<pH_{zpc}}}{\longleftrightarrow} \mathrm{S-O^-+H_2O} \tag{11}$$

Here, S–OH, $\mathrm{S{-}OH_2^+}$, and S–O– represent neutral, protonated, and deprotonated surface hydroxyl groups, respectively. According to Eqs. (10) and (11), when the solution pH is less than the $\mathrm{pH_{zpc}}$ of the catalyst, the surface hydroxyl groups on the metal oxide will be in their protonated form, and, when the pH is greater than $\mathrm{pH_{zpc}}$, the surface hydroxyl groups on the metal oxide will be in their deprotonated form. Moreover, when the pH is close to the $\mathrm{pH_{zpc}}$, the surface hydroxyl groups will be in a neutral charge state. Therefore, because the solution pH will likely influence the iron silicate-catalyzed ozonation, it is necessary to investigate the influence of the solution pH on catalytic ozonation in the presence of iron silicate (60℃), iron silicate (250℃), iron silicate (600℃), and iron silicate (800℃).

The influence of solution pH on pCNB degradation was investigated for the ozone alone, O_3/iron silicate (60℃), O_3/iron silicate (250℃), O_3/iron silicate (600℃), and O_3/iron silicate (800℃) systems, and the results are shown in Fig. 4. As shown in the figure, the solution pH significantly affects the degradation of pCNB, and a single inflexion point is observed in the response curve of each catalytic ozonation system, which indicates the point of maximum impact on the ozonation degradation of pCNB over a pH range 3–10.5. The inflexion points appeared for solution pH values of 7.1, 7.9, 8.3, and 8.7 for iron silicate (60℃), iron silicate (250℃), iron silicate (600℃), and iron silicate (800℃), respectively. As shown in Table 1, the $\mathrm{pH_{zpc}}$ values for iron silicate (60℃), iron silicate (250℃), iron silicate (600℃), and iron silicate (800℃) are 7.04, 7.73, 8.21, and 8.64, respectively. This indicates that, when the solution pH was near to the iron silicate $\mathrm{pH_{zpc}}$, the iron silicate surface and surface hydroxyl groups were at neutral charge states, which correlated with the high catalytic activity described above. From the above analysis, it can be concluded that neutral surface hydroxyl species were more active in the catalyzed ozonation process than protonated and deprotonated surface hydroxyl species.

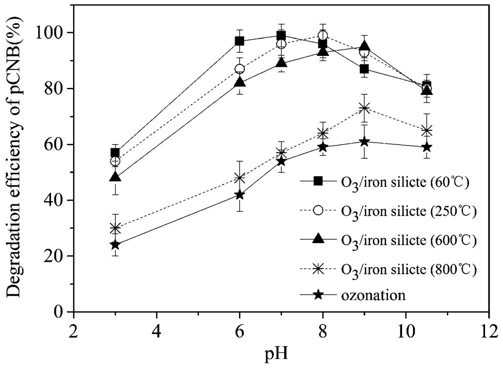

Fig. 4. Effect of pH on the degradation of pCNB. Experimental conditions: $[\mathrm{pCNB}]_0 = 100$ μg L^{-1}; $[O_3]_0 = 0.6$ mg L^{-1}; [iron silicate] = 100 mg L^{-1}; solution pH 7.0; reaction time = 15 min; $T = 298$ K.

3.6. Discussion regarding the mechanism of iron silicate catalytic ozonation of pCNB

To investigate the mechanism of iron silicate catalytic ozonation, we must first discuss the composition of the iron silicate in detail.

Sodium silicate is an ionic compound, and the strong base weak acid salt when dissolved in water can increase the pH value of the solution according to the following equations [25]:

$$SiO_3^{2-} + H_2O \rightarrow H_2SiO_4^{2-} + HSiO^{3-} \tag{12}$$

$$H_2SiO_4^{2-} + H_2O \rightarrow H_3SiO^{4-} + OH^- \tag{13}$$

FeOOH can be prepared based on the following reaction [26]:

$$Fe^{3+} + 3OH^- \rightarrow FeOOH^+H_2O \tag{14}$$

It is well known that an $Fe(NO_3)_3$ solution is acidic. When an Na_2SiO_3 solution is mixed with a solution of $Fe(NO_3)_3$, the above reactions (12), (13), and (14) occur simultaneously, and FeOOH and $Si(OH)_4$ are formed instantly *in situ*, as shown by Ali et al. [26]. Swedlund and Webster [27] reported that, when $Si(OH)_4$ contacts with FeOOH, silicato-iron(III) surface complexes between Si and Fe are likely to form, according to the following scheme: (a) Fe–O–Si (OH); (b) Fe–O$(OH)_2$–Si$(OH)_3$; or (c) (OH)Si–Fe–(OH) O–O–O(OH)–Fe–Si(OH). Based on the above analysis, the synthesized iron silicate impregnates the Fe_2O_3, $Si(OH)_4$, FeOOH, and silicato-iron(III) surface complexes. The results of XRD and XRF (not shown) confirm the above analysis, and the results demonstrate that iron silicate (60℃) was composed of amorphous Fe_2O_3·(SiO_2)4.17·(H_2O)10.7, iron silicate (250℃) was composed of amorphous Fe_2O_3·(SiO_2)4.17·(H_2O)2.1, iron silicate (600℃) was composed of amorphous Fe_2O_3·(SiO_2)4.17, and iron silicate (800℃) was composed of a new crystalline phase of Fe_2SiO4, which indicates that, when the drying temperature of iron silicate was 800℃, most of the Fe_2O_3 could react with SiO_2 to form Fe_2SiO_4. As shown in Fig. 1, the catalytic activity of iron silicate (800℃) was much lower than those of iron silicates dried at lower temperatures, which suggests that Fe_2O_3, $Si(OH)_4$, SiO_2, FeOOH, and silicato-iron(III) surface complexes are the active components in the iron silicate catalytic ozonation process, and may have a synergistic effect on catalytic ozonation for the degradation of pCNB in aqueous solution. To isolate the primary active ingredient of iron silicate in the catalytic ozonation process, SiO_2, Fe_2O_3, FeOOH, and $Si(OH)_4$ were employed as catalysts in the catalytic ozonation of pCNB for comparison.

As shown in Fig. 5, SiO_2 and $Si(OH)_4$ have no catalytic activity for the ozonation of pCNB. However, Fe_2O_3 and FeOOH have a significant impact on pCNB degradation, but their catalytic activities are both lower than that of iron silicate dried at 60℃. Combining the results of Figs. 1 and 5, it can be concluded that Fe_2O_3, FeOOH, and silicato-iron(III) surface complexes may be the predominant effective components of catalytic activity in the iron silicate catalytic ozonation of pCNB.

It is interesting to note that the hydroxyl groups on the catalyst surface play an important role in the formation of ·OH from ozone decomposition during heterogeneous catalytic ozonation [28]. It is generally believed that dissolved ozone firstly adsorbs onto the surface of the catalysts, and then decomposes rapidly due to the presence of surface hydroxyl groups. The formation of ·OH can oxidize organic compounds either in solution, on the catalyst surface, or in a thin film layer above the surface [29]. As discussed in Section 2.5, the neutral surface hydroxyl groups determined the catalytic activity of iron silicate in the degradation of pCNB. As demonstrated in Figs. 1 and 3, the catalytic activity decreased with increasing drying temperature, although the primary composition of the iron silicate remained constant. Combined with the results of Table 1 and Fig. 4, we can conclude that this difference may be derived from the different densities of hydroxyl groups on the surfaces of the iron silicates, and that increasing surface hydroxyl group density enhanced the pCNB degradation reaction rate remarkably. Therefore, we can conclude that the

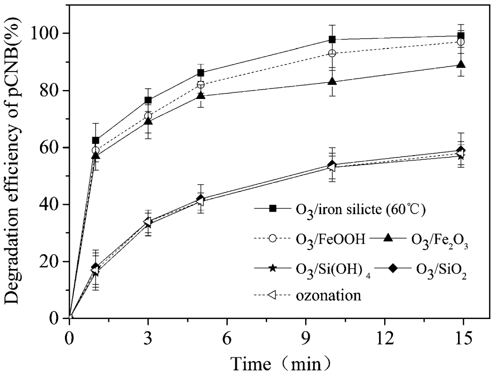

Fig. 5. Degradation of pCNB with respect to ozonation time for isolated catalyst components. Experimental conditions: $[pCNB]_0$ = 100 μg L^{-1}; $[O_3]_0$ = 0.6 mg L^{-1}; [catalyst] = 100 mg L^{-1}; solution pH 7.0; T = 298 K.

surface hydroxyl group was the active site for the catalytic ozonation process.

4. Conclusions

The use of iron silicate dried at 60℃ significantly enhances the degradation efficiency of pCNB in aqueous solution by catalytic ozonation relative to ozonation alone. The results indicate that the increased degradation efficiency relative to ozonation alone can scarcely be attributed to the adsorption of pCNB on the surface of iron silicate. The investigation of the reaction mechanism indicates that an increasing iron silicate drying temperature up to 800℃ may change the composition of the iron silicate, resulting in a progressively decreased catalytic activity. Fe_2O_3, FeOOH, and silicato-iron(III) surface complexes may be the predominant effective components of catalytic activity in the iron silicate catalytic ozonation of pCNB. Decreasing the drying temperature of iron silicate creates an increased density of surface hydroxyl groups, resulting in the acceleration of ozone decomposition and the formation of ·OH, leading to an increased degradation efficiency of pCNB in aqueous solution.

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