Study on the relationship between the decomposition rate of ozone and the removal rate of MTBE in catalytic ozonation

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Abstract: This work investigated the relationship between the decomposition rate of ozone and the removal rate of MTBE within a continuous reactor. The effects of different residence time, initial ozone dose and different catalysts on ozone decomposition and MTBE degradation in catalytic ozonation were evaluated. The results indicate that the removal rate of MTBE increased with the increasing of the residence time and initial ozone dose by the catalysts used in the experiments. But the decomposition rate of ozone showed different tends; it increased with the increasing of the residence time and initial ozone dose in the presence of iron hydroxide and emerged a peak at residence time of 5.7 min in the presence of cerium dioxide. No correlation could be established between the decomposition rate of ozone and the removal rate of MTBE in catalytic ozonation because of the mechanisms of catalytic oxidation in the presence of different catalysts. The results of this study could also help us to provide specific reference for catalysts selection and some running parameters of catalytic ozonation for degrading MTBE.

Key words: catalytic ozonation; methyl tert-butyl ether; ozone decomposition; cerium dioxide

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0 Introduction

Ozone has recently received much attention in water treatment because of its high oxidation and disinfection potential, and it has been used in many drinking water plants for the oxidation to improve taste and colour as well as to remove the organic and inorganic compounds in water. Despite several advantages of using ozone, it has a few disadvantages, which limit its application in water treatment. The main disadvantage is partial and selective oxidation of organic compounds present in water. So, different ozone catalysts were used to improve the oxidation efficiency. Catalytic ozonation was found to be effective for the removal of several organic compounds from the drinking water. The homogeneous catalytic ozonation and heterogeneous catalytic ozonation usually be considered to be the main catalytic ozonation processes. The heterogeneous catalytic ozonation processes usually be taken in the presence of metal oxides or metals/metal oxides on supports[1].

However, the relationship between the decomposition rate of ozone and the removal rate of organic matters in catalytic ozonation was not well studied. It was usually considered that the removal rate of organic matters increased

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with the increasing of the decomposition rate of ozone, but there might be different mechanisms in catalytic ozonation with different catalysts and the decomposition rate of organic matter might be different. So the relationship of the decomposition rates of ozone and the decomposition rates of MTBE was discussed in this paper. In order to be close to the use of the catalysts, experiments were carried out within a continuous reactor.

1 Materials and methods

1.1 Materials

The catalysts used in the experiments were as follows: iron hydroxide (FeOOH) supported on natural zeolite; high silica zeolites; magnesia (MgO) supported on activated alumina; cerium dioxide (CeO_2) supported on activated alumina and activated alumina. The catalysts were washed with distilled water before they were used until the pH of the washed water was equal to the raw water, and then catalysts were dried at 100 ℃ before use.

The stock solution of MTBE (10 g• L^{-1}) was diluted to a concentration of 2 mg• L^{-1} by distilled water which was adjusted to a set pH value (7.0±0.1) by adding dilute NaOH. Ozone was produced by an ozone generator for laboratory purposes. The source of ozone generator was the pure oxygen.

1.2 Experimental system

In order to simulate to the realistic situation, experiments were carried out in circular continuous flow reactors. O_2/O_3 gas mixture was bubbled continuously through the reactor I containing the distilled water at a set pH value (7.0±0.1). The ozone water flowed into reactor II by gravity and mixed quickly with 2 mg• L^{-1} MTBE solution in reactor II, then flowed into reactor III. 1 mL of 0.1 mol• L^{-1} H_2SO_4 solution and 0.6 mL of 0.04 mol• L^{-1} $Na_2S_2O_3$ solutions were added into colorimetric tube. The solution samples from the outlet were taken and added into colorimetric tube to 50 mL, then the solutions was extracted by 10 g of Na_2SO_4 and 3 mL of *n*-PTL.

All experiments were performed at (20±2) ℃. Different initial dissolved ozone concentrations could be set by varying the ozone gas concentration and working current of ozone generator. Glass sand core was used to support the catalysts bed in the reactor III.

1.3 Analysis

The concentration of MTBE was determined by gas chromatograph (Agilent 4890D, GC-FID) with 1 mL of splitless injection.

The ozone content in distilled water was determined by ultraviolet spectrophotometer (752)[2].

2 Results and discussion

2.1 Effect of residence time on ozone decomposition and oxidation of MTBE

Fig 1 and Fig 2 showed the effect of residence time on ozone consumption and the removal rate of MTBE in the presence of FeOOH and CeO_2 respectively. The experiments were carried out at (20±2) ℃ and pH (7.0±0.1).

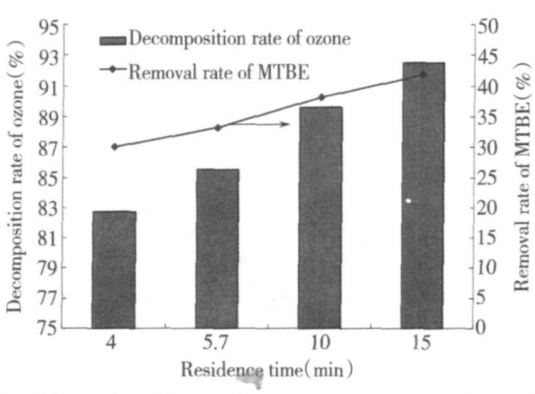

Fig. 1 Effect of residence time on ozone consumption and the removal rate of MTBE in the presence of FeOOH

(pH_0=(7.0±0.1), T=(20±2) ℃, $[O_3]_0$=4.0 mg•L^{-1}, C_{MTBE}=2.0 mg•L^{-1})

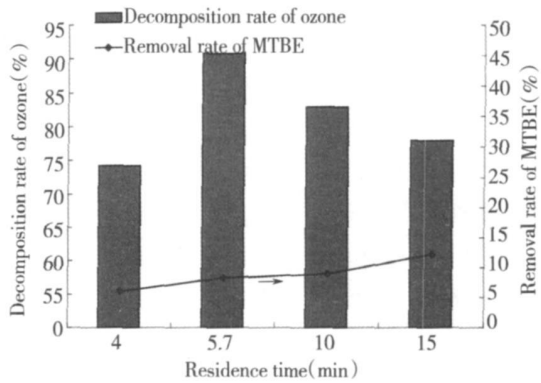

Fig. 2 Effect of residence time on ozone consumption and the removal rate of MTBE in the presence of CeO_2

(pH_0=(7.0±0.1), T=(20±2) ℃, $[O_3]_0$=4.0 mg•L^{-1}, C_{MTBE}=2.0 mg•L^{-1})

Generally, it was considered that the longer the residence time was, the higher the removal rate of organic matters was, but the influence of the residence time on ozone decomposition was rarely studied. From the result in the Fig. 1, the removal rate of MTBE and the decomposition rate of ozone increased with the increasing of the residence time; it showed that the most of MTBE and ozone were removed when the residence time was at four minutes and the removal rate changed little because of the lower concentration of ozone in water with the increasing of the residence time. Our privious study proved that iron hydroxide could catalyze ozone to induced hydroxyl radicals, the most of organic matters were removed in two minutes by catalytic ozonation with iron hydroxide catalyst. Under our experimental condition, the high removal rate of MTBE and decomposition rate of ozone showed the high catalytic activity of iron hydroxide.

Compared with the catalytic ozonation of iron hydroxide, the removal rate of MTBE was lower and the peak of the decomposition rate of ozone emerged at residence time of 5.7 min in the presence of cerium dioxide. The reason of above might be the sorption, desorption and decomposition of ozone appeared simultaneously on CeO_2, therefore, the removal rate of ozone on CeO_2 emerged a peak as the increasing of the residence time. A further study would be taken to learn about the mechanisms of ozone decomposition on CeO_2.

2.2 Effect of initial ozone dose on ozone decomposition and oxidation of MTBE

Fig. 3 and Fig. 4 showed the effect of ozone dose on ozone consumption and the removal rate of MTBE in the presence of FeOOH and MgO respectively. The experiments were also carried out at (20 ±2) ℃, pH (7.0 ±0.1) and the flow rate 0.85 m• h^{-1}.

The initial concentration of ozone plays an important role in the removal rate of the organic matters during the catalytic ozonation from the Fig. 3, the decomposition rate of ozone rarely changed and were all above 90% at different initial concentration of ozone. The removal rate of MTBE increase fast with the increasing of ozone concentration, and nearly 40% of MTBE were removed at 4.83 mg• L^{-1} of initial concentration of ozone. The results suggested the high catalytic activity of iron hydroxide. There were enough surface active sites on the iron hydroxide that catalyze ozone decomposition and the removal of MTBE under our experimental conditions. But from the catalytic ozonation of other catalysts, the decomposition rate of ozone might decrease with the increasing of ozone concentration when the active sites were not enough for catalytic ozone decomposition, which would be taken in further study.

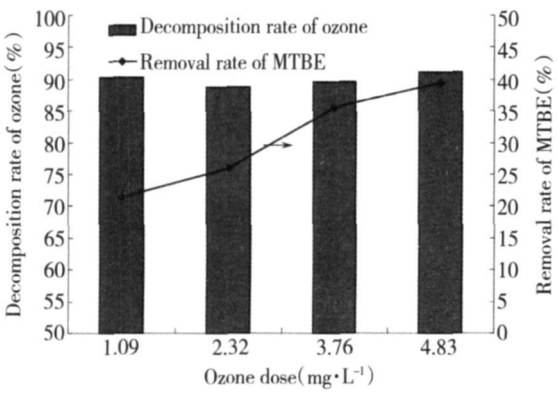

Fig. 3 Effect of ozone dose on ozone consumption and the removal rate of MTBE in the presence of FeOOH

(pH_0=(7.0 ± 0.1), T=(20 ± 2) ℃, V=0.85 m·h^{-1}, C_{OMTBE}=2.0 mg·L^{-1})

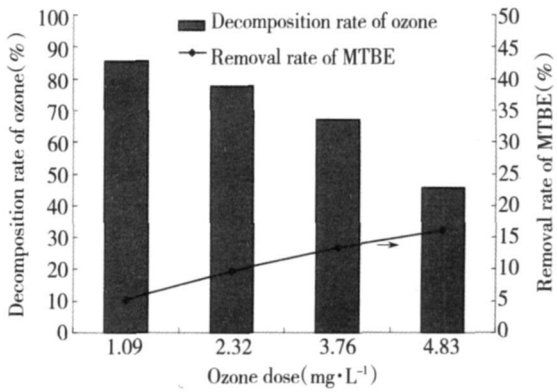

Fig. 4 Effect of ozone dose on ozone consumption and the removal rate of MTBE in the presence of MgO

(pH_0=(7.0 ± 0.1), T=(20 ± 2) ℃, V=0.85 m·h^{-1}, C_{OMTBE}=2.0 mg·L^{-1})

Contrary to iron hydroxide, the decomposition rate of ozone decreased significantly with the increasing of ozone concentration, the decomposition rate of ozone and the removal rate of MTBE acted differently (Fig. 4). The decomposition rate of ozone was only 47% at 4.83 mg• L^{-1} of initial concentration of ozone. The reason above was that ozone decomposed more slowly than the increasing of the initial concentration of ozone, so the decomposition rate of ozone decreased significantly with the increasing of ozone concentration. Under the same initial concentration of MTBE, the increasing of ozone concentration could improve reaction rate between ozone and MTBE, so the re-

moval rate of MTBE increased with the increasing of the initial ozone concentration which was the same as the phenomenon above.

Magnesia showed weak catalytic activity in catalytic ozonation, but it might be used for combining with other catalysts because of the enough ozone concentration in the outlet solution.

2.3 Comparison of ozone decomposition and oxidation of MTBE by different catalysts

Fig. 5 and Fig. 6 showed the decomposition rate of ozone and the removal rate of MTBE catalyzed by several catalysts at flow rate of 0.85 $m \cdot h^{-1}$ and 1.49 $m \cdot h^{-1}$ respectively. The experiments were also carried out at (20±2) ℃ and pH (7.0±0.1).

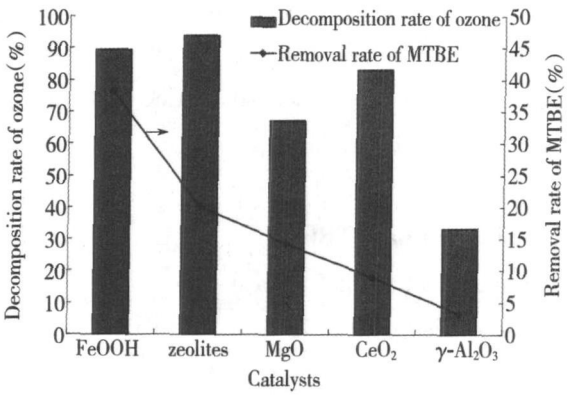

Fig. 5 The decomposition rate of ozone and the removal rate of MTBE catalyzed by several catalysts at flow rate of 0.85 $m \cdot h^{-1}$

(pH_0=(7.0±0.1), T=(20±2) ℃, $[O_3]_0$=4.0 $mg \cdot L^{-1}$, C_{OMTBE}=2.0 $mg \cdot L^{-1}$)

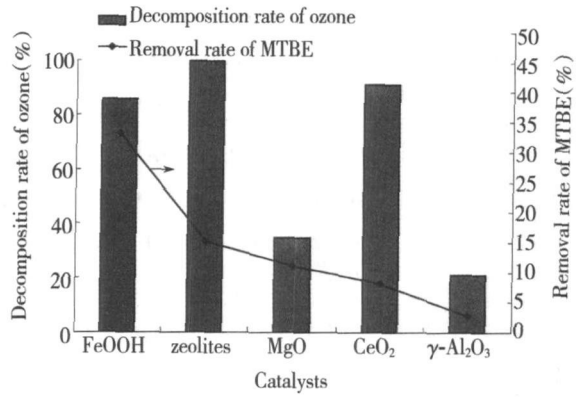

Fig. 6 The decomposition rate of ozone and the removal rate of MTBE catalyzed by several catalysts at flow rate of 1.49 $m \cdot h^{-1}$

(pH_0=(7.0±0.1), T=(20±2) ℃, $[O_3]_0$=4.0 $mg \cdot L^{-1}$, C_{OMTBE}=2.0 $mg \cdot L^{-1}$)

Under the same condition, the order of ozone decomposition rate by different catalysts was as follows: high silica zeolites> iron hydroxide (FeOOH) > cerium dioxide (CeO_2) > magnesia (MgO) > active alumina (γ-Al_2O_3). The order of the removal rates of MTBE by different catalysts was as follows: iron hydroxide (FeOOH) > high silica zeolites> magnesia (MgO > cerium dioxide (CeO_2) > active alumina (γ-Al_2O_3). The removal rate of MTBE by catalytic ozonation was not proportional to the decomposition rate of ozone in the presence of different catalysts.

It is now widely assumed that ozone reacts in aqueous solution on various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving the hydroxyl radical induced by the ozone decomposition in water. For heterogeneous catalytic ozonation in the presence of solid catalysts, it is generally considered that there are three possible mechanisms[1]: (1) Chemisorption of ozone on the catalyst surface leading to the formation of active species which react with non-chemisorbed organic molecule. The hydroxyl radical and some other radical species are generally induced by catalytic ozonation. The mechanism of catalytic ozonation in the presence of iron hydroxide is just this mechanism[3-4]. The hydroxyl radicals that are highly reactive and non-selective and can react with almost all types of organics and inorganics are induced after adding iron hydroxide into aqueous ozone system. (2) Chemisorption of organic molecule (associative or dissociative) on the catalytic surface and its further reaction with gaseous or aqueous ozone. The small molecular organic acids complex with metallic oxide on the surface in some certain conditions and the complexing organic molecule is easy to be oxidized by ozone directly. The mechanism of catalytic ozonation in the presence of cerium dioxide is just this; cerium dioxide can complex with the organic acid to enhance the removal of the organic acid. (3) Adsorption of both ozone and organic molecules and the subsequent interaction between chemisor species. The weak polar organic matters and ozone are enriched on the nonpolar surface at the same time. The mechanism of catalytic ozonation in the presence of high silica zeolites is just this mechanism, adsorption of both ozone and organic molecules increases the removal of the organic matters[5-6].

The different catalysts processes showed the different catalytic ozonation mechanisms, so they showed differ-

ent ability of degradation of organic compounds and decomposition of ozone in aqueous solution. The removal rate of MTBE by catalytic ozonation was not proportional to the decomposition rate of ozone in the presence of different catalysts.

3 Conclusions

The aim of this paper was to investigate the relationship between the decomposition rate of ozone and the removal rate of MTBE. For the different catalytic ozonation mechanisms with different catalysts, the improvement of the decomposition of ozone by catalysts did not mean better decomposition of the organic matter by catalytic ozonation.

Iron hydroxide showed the highest catalytic activity in ozone decomposition and removal of MTBE. The removal rate of MTBE increased with the increasing of the residence time and initial ozone dose by the above catalysts. But the decomposition rate of ozone showed different tends: it increased with the increasing of the residence time and initial ozone dose in the presence of iron hydroxide; decreased in the presence of magnesia with the increasing of initial ozone dose and emerged a peak at residence time of 5.7 min in the presence of cerium dioxide.

In a word, the higher decomposition rate of ozone did not mean the higher removal rate of MTBE because of the different mechanisms of catalytic oxidation, the results of this study could also help us to provide specific reference for catalysts selection and some running parameters of catalytic ozonation for degrading MTBE.

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References

[1] KASPRZYK-HORDERN B, ZIÓLEK M, NAWROCKI J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment [J]. Applied Catalysis B: Environmental, 2003, 46: 639-669.

[2] BADER H, HOIGNÉ J. Determination of ozone in water by the indigo method [J]. Water Research, 1981, 15(4): 449-456.

[3] ZHANG T, CHEN Z L, MA J, et al. Catalytic ozonation of trace nitrobenzene in water by iron hydroxide[J]. Environmental Science, 2004, 25(4): 43-47.

[4] MA J, ZHANG T, CHEN Z L, et al. Pathway of aqueous ferric hydroxide catalyzed ozone decomposition and ozonation of trace nitrobenzene [J]. Environmental Science, 2005, 26(2): 78-82.

[5] FUJITA H, IZUMI J, SAGEHASHI M, et al. Adsorption and decomposition of water-dissolved ozone on high silica zeolites [J]. Water Research, 2004, 38: 159-165.

[6] ANDERSON M A. Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites [J]. Environmental Science and Technology, 2000, 34(4): 725-727.

臭氧催化氧化过程中臭氧分解与 MTBE降解速率关系研究

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摘　要: 通过连续流实验考察了催化氧化过程中臭氧分解与甲基叔　基醚(MTBE)降解速率之间的关系, 同时讨论了停留时间、初始臭氧浓度以及不同催化剂对臭氧分解以及 MTBE降解速率的影响。结果显示, 随着停留时间以及初始臭氧浓度的增加, MTBE的去除率呈增加趋势; 羟基氧化铁催化臭氧分解时, 臭氧分解速率随着停留时间以及初始臭氧浓度的增加而增加, 二氧化铈催化臭氧分解速率在停留时间为 5.7 min时最大。由于不同催化剂催化臭氧机理不同, 所以臭氧分解与 MTBE的去除没有什么相关性, 并不是臭氧分解越快 MTBE的去除率越高。臭氧催化氧化过程中催化剂以及运行参数的选择提供了参考。

关键词: 臭氧催化氧化; 甲基叔　基醚; 臭氧分解; 二氧化铈