

# Degradation of nitrobenzene in aqueous solution by ozone-ceramic honeycomb

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**Abstract:** The degradation of nitrobenzene by ceramic-honeycomb catalyzed ozonation was investigated. The results showed that the presence of ceramic honeycombs significantly increased the oxidation rate of nitrobenzene by ozone compared to the case of ozone oxidation alone. In this paper, the effects of various factors on the catalytic oxidation were investigated, such as the amount of catalysts, the ozone dosage, the temperature, the pH value and the presence of *tert*-butanol. With the addition of *tert*-butanol the removal of nitrobenzene decreased sharply, which appeared to support that, the degradation of nitrobenzene by ozonation followed a radical type mechanism. The EPR experiments verified that higher nitrobenzene removal rate was attributed to more OH<sup>•</sup> radicals generated in the catalyzed ozonation than ozonation alone.

**Keywords:** ozone; catalytic ozonation; ceramic-honeycomb; nitrobenzene; advanced oxidation; water treatment

## Introduction

As a promising advanced oxidation technology for water treatment, catalytic ozonation has received great attention for the efficient degradation of organic compounds in recent years (Legube, 1999). Some studies showed that homogeneous and heterogeneous catalysts were effective for removing contaminants from water (Cooper, 1999; Andreozzi, 2000; David, 2002). It was believed that the heterogeneous catalytic ozonation could be easily applied in drinking water purification and wastewater treatment, thus received more attentions. It was reported that MnO<sub>2</sub> formed *in situ* exhibited high activity for ozonation of atrazine compared to the case of ozonation alone, it was also indicated that humic substances and radical scavengers influenced the degradation of atrazine. After continuous investigations, the results suggested the generation of hydroxyl radical via ozone reacting with the surface-bound OH ions on the surface of manganese dioxide (Ma, 1997; 1999; 2000). The use of TiO<sub>2</sub> as catalysts for the ozonation of oxalic acid in water significantly improved its removal compared to non-catalytic ozonation and led to higher degree of mineralization of the compound. The mechanism of free radical generated on TiO<sub>2</sub> surface from decomposition-desorption of ozone was proposed (Beltrán, 2002). Recent study indicated that alumina was an effective heterogeneous catalyst for the ozonation of refractory organic compounds such as oxalic, acetic and salicylic acids. Higher DOC removal has been obtained in the presence of Al<sub>2</sub>O<sub>3</sub>, accordingly, a reaction pathway was presented by which ozone reacted with OH ions on the surface of catalyst and thus the radical species were formed (Mathias, 2004).

As mentioned above, several metal-oxide catalysts such as MnO<sub>2</sub>, TiO<sub>2</sub> or transition metals deposited on porous supports were repeatedly conducted on the efficiency in catalytic ozonation. Therefore, selection or preparation of active catalysts was the key point to develop catalytic ozonation, the present paper focused on the catalytic activity of cordierite-ceramic honeycomb, which is often used as a carrier material for metal or metal oxide catalysts for vehicular (Agrafiotis, 2000; Kikuchi, 2001; Qu, 2004). But ceramic honeycombs have rather been neglected as to their chemical and morphological properties for catalytic ozonation reaction in aqueous solution. The main objective of this study was to

apply a patented catalyst to ozonation system and to investigate the degradation efficiency of refractory organic compounds in aqueous solution (Ma, 2003).

## 1 Experimental

### 1.1 Materials

Cordierite ceramic honeycombs were applied in this system (Shanghaipengyi Material Co. Ltd., China). Monolithic honeycomb is cylindrical (50 mm in diameter and 50 mm in length), and the cell densities of ceramic honeycombs are 400 square cells per square inch. The crystal phase of ceramic (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) was analyzed by X-ray power diffraction (XRD), and its specific surface area (0.35 m<sup>2</sup>/g) was measured using Brunauer Emmett and Teller (BET) through low-temperature nitrogen adsorption. Ceramic honeycombs were rinsed with detergent to remove impurities and then dried at 80°C before ozonation experiment.

The model water was prepared by diluting nitrobenzene pre-distilled (with purity of 99.80%, Beijing Chemical Industrial Factory, China) in distilled water until the concentration was obtained. Sulfuric acid and sodium hydroxides (analytical grade) were added in the aqueous solution to control the pH. The pH did not vary more than five decimal units after experiments, so the experiments were conducted in non-buffered solution. Other chemical reagents used in the experiment, such as sodium thiosulphate solution and *tert*-butanol, are analytical grade reagents.

### 1.2 Analytical methods

The concentration of nitrobenzene in reaction process was analyzed by GC-14C gas chromatography (Shimadzu Corporation, Japan). The pH of aqueous solution measured by Delta 320 pH meter (Shanghai REX Instrument Factory, China). The total production of ozone and effluent gas were measured by iodometry method (Ozone Standards Committee Method). Dissolved ozone in the water was detected by spectrophotometer using the Indigo method (Bader, 1981). The consumed ozone was obtained by the following calculation: consumed ozone = introduced ozone - (ozone in off-gas + ozone residual in water).

EPR experiment (Bruker Elexsys E500 ESR spectroscopy) was applied with powdered ceramic as catalysts. Spin-trapping reagent DMPO (5, 5-dimethyl-1-

pyrolytic-N-oxide) was used in the process. EPR measurements were conducted under the conditions: microwave power 20 mW; modulation frequency 100 kHz; sweep width 100.0 G; central magnetic field 3480 G.

### 1.3 Ozonation procedure

Experiments were carried out in a cylindrical reactor (inside diameter of 50 mm and capacity of 3.0 L) made of stainless steel (Fig. 1), which is shielded to control reaction temperature by circulating water. Before the experimental operation, the reactor was pre-ozonated for 4 min and washed several times with distilled water to minimize the potential side effects. In this experiment, the model water (3 L) was pumped into the column by a magnetic pump (Xishan Pump Co. Ltd., Shanghai, China) and then circulated. The ozone was generated from ozone generator (Tsinghuatonghui Co. Ltd., China) and was fed into the reactor via a porous filter at bottom of column. The cordierite honeycomb catalyst was properly placed on the porous filter before oxidation reaction. The ozonation time was controlled at 10 min for all the samples. Water samples were taken from the contactor column at every 2 min (each 80 ml) to analyze the concentration of residual nitrobenzene.

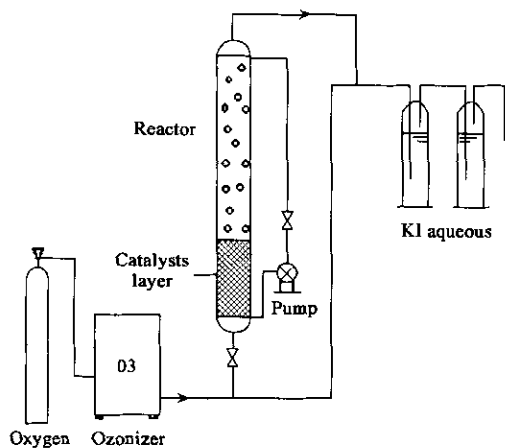


Fig. 1 Schematic diagram of ceramic-honeycomb catalyzed ozonation system

## 2 Results and discussion

### 2.1 Influence of ceramic honeycombs on the ozonation rate of nitrobenzene

In the present study, nitrobenzene was selected because of its refractory nature to conventional ozonation processes ( $K_{O_3} = 0.09 \pm 0.02 \text{ mol}/(\text{L}\cdot\text{s})$ ), but it can be degraded by OH radicals due to its high reactivity with OH ( $K_{OH} = 3.9 \times 10^9 \text{ mol}/(\text{L}\cdot\text{s})$ ; Legube, 1999), so nitrobenzene can be selected as a probe compound for hydroxyl radical measurement. As can be seen from Fig. 2, under the conditions investigated, catalytic ozonation leads to about 80% nitrobenzene conversion after 10 min of reaction. In contrary, nitrobenzene adsorption process and ozonation alone result in only 10% and 20% reduction of nitrobenzene respectively. It is also seen from the variation of the residual ozone concentration that the consumption of ozone in the presence of catalysts was higher than ozonation alone, and more ozone were consumed with higher catalyst dosage used. From Fig. 2 and Fig. 3, it is expected that nitrobenzene can be adsorbed on ceramic honeycomb surface, but not obvious.

In the presence of ozone alone, however, the limited degradation of nitrobenzene was achieved for its refractory nature. In contrast, with ceramic honeycombs applied, the ozonation rate of nitrobenzene was increased. It is expected that OH radicals were possibly produced in catalytic oxidation process, because the removal efficiency of nitrobenzene increased significantly. When higher catalyst dosage used, greater removal of nitrobenzene can be achieved with more ozone being consumed. This indicates, possibly, that ceramic honeycombs decomposed ozone to generate hydroxyl radicals, thereby causing the degradation of nitrobenzene.

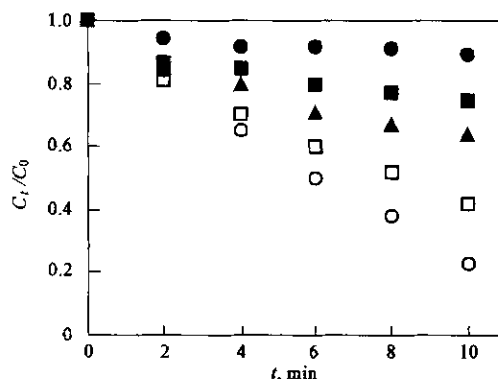


Fig. 2 Degradation of nitrobenzene in ozonation and catalytic ozonation experiments

Conditions: temp.  $21 \pm 1^\circ\text{C}$ ; pH 6.80; initial nitrobenzene concentration: 50  $\mu\text{g}/\text{L}$ ; total ozone applied: 1.5  $\text{mg}/\text{L}$ ; background: distilled water. ●: nitrobenzene adsorption on ceramic honeycombs (5 blocks of honeycombs used); ■: non-catalytic ozonation of nitrobenzene; ▲: catalytic ozonation of nitrobenzene (1 block of honeycomb); □: catalytic ozonation of nitrobenzene (3 blocks of honeycombs); ○: catalytic ozonation of nitrobenzene (5 blocks of honeycombs)

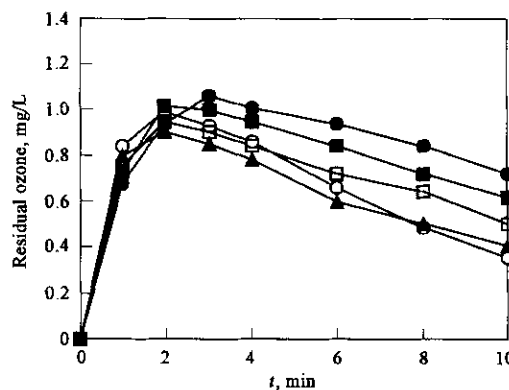


Fig. 3 Residual ozone concentration in oxidation processes

Conditions: temp.  $21 \pm 1^\circ\text{C}$ ; pH 6.80; initial nitrobenzene concentration: 50  $\mu\text{g}/\text{L}$ ; total ozone applied: 1.5  $\text{mg}/\text{L}$ ; background, distilled water. ●: ozonation alone; ■: catalytic ozonation with 1 block of ceramic honeycomb; □: catalytic ozonation with 3 blocks of ceramic honeycombs; ○: catalytic ozonation with 5 blocks of ceramic honeycombs in the presence of t-butonal (8  $\text{mg}/\text{L}$ ); ▲: catalytic ozonation with 5 blocks of ceramic honeycombs

### 2.2 Influence of current velocity on the ozonation rate of nitrobenzene

Heterogeneous catalytic ozonation of nitrobenzene is a gas-liquid-solid reaction, so the mass transfer and chemical steps may affect the degradation rate. With monolithic catalyst used in liquid ozonation system, however, considering its special structure, cylindrical ceramic honeycombs may influence the mass transfer of ozone from the

gas phase to the liquid phase. Therefore, in order to investigate the reaction mechanism involving adsorption, oxidation and desorption process, it is necessary to confirm that the reactions are carried out under chemical control conditions. In the circulation process performed by magnetic pump, current velocity is the maximum factor influencing the mass transfer. Cylindrical ceramic honeycombs with rectangular channels is beneficial to cause uniform distribution of ozone solubility, however, under an appropriate current velocity, the effect of ceramic honeycombs on ozone transfer can be negligible. As shown in Fig. 4, when current velocity is higher than 100 L/h, it leads to slight improvement of the nitrobenzene removal rate. Hence, the external mass transfer resistance (gas to liquid and liquid to solid mass transfer) may be neglected when current velocity higher than this value. Additionally, it can be assumed that there is no internal mass-transfer limitation because monolithic catalysts were used (contrary to the powdered form). Consequently, it can be considered that the catalytic ozonation process was chemically controlled when performed at current velocity of 100 L/h.

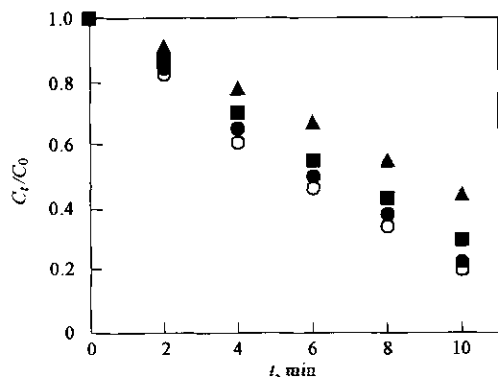


Fig. 4 Degradation of nitrobenzene under different current velocities  
Conditions: temp.  $21 \pm 1^\circ\text{C}$ ; pH 6.80; initial nitrobenzene concentration:  $50 \mu\text{g/L}$ ; total ozone applied:  $1.5 \text{ mg/L}$ ; number of ceramic honeycombs used: 5 blocks; background: distilled water; circulating speed:  $\blacktriangle$ : 50 L/h;  $\blacksquare$ : 80 L/h;  $\bullet$ : 100 L/h;  $\circ$ : 120 L/h

### 2.3 Influence of nitrobenzene and ozone concentration

Fig. 5 and Fig. 6 present respectively the effect of initial concentration of ozone and nitrobenzene on the nitrobenzene degradation rate. It is observed that the ozone concentration has a positive function on the nitrobenzene degradation, especially for concentration less than  $1.5 \text{ mg/L}$ . However, there is little improvement of nitrobenzene conversion by increasing total ozone applied from  $1.5 \text{ mg/L}$  to  $2.5 \text{ mg/L}$ . Additionally, the degradation rate of nitrobenzene is slightly affected by its initial concentration shown in Fig. 6. Based on nitrobenzene degradation rate from Fig. 5 and Fig. 6 both variables influence positively on the degradation rate.

### 2.4 Influence of temperature on the ozonation rate of nitrobenzene

As shown in Fig. 7 the temperature is an important factor for the degradation of nitrobenzene. In the present system, temperature is positive to oxidation reaction from 10 to  $40^\circ\text{C}$ . The increase of temperature from 10 to  $30^\circ\text{C}$  leads to a significant increase of nitrobenzene conversion but only a slight enhancement is observed when temperature is further increased up to  $40^\circ\text{C}$ . This result may be due to the effect of

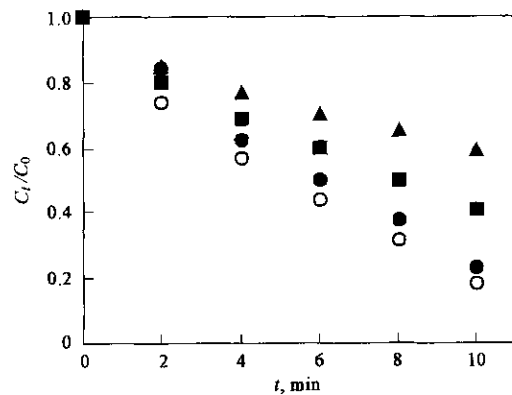


Fig. 5 Degradation of nitrobenzene during catalytic ozonation with different total ozone applied

Conditions: temp.  $21 \pm 1^\circ\text{C}$ ; pH 6.80; initial nitrobenzene concentration:  $50 \mu\text{g/L}$ ; number of ceramic honeycombs used: 5 blocks; background: distilled water; total ozone applied:  $\blacktriangle$ :  $0.5 \text{ mg/L}$ ;  $\blacksquare$ :  $1.0 \text{ mg/L}$ ;  $\bullet$ :  $1.5 \text{ mg/L}$ ;  $\circ$ :  $2.5 \text{ mg/L}$

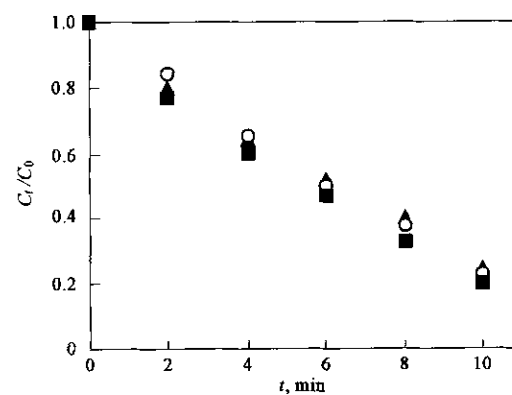


Fig. 6 Degradation of nitrobenzene during catalytic ozonation at different initial nitrobenzene concentrations

Conditions: temp.  $21 \pm 1^\circ\text{C}$ ; pH 6.80; total ozone applied:  $1.5 \text{ mg/L}$ ; number of ceramic honeycombs used: 5 blocks; background: distilled water; initial nitrobenzene concentration:  $\blacktriangle$ :  $50 \mu\text{g/L}$ ;  $\circ$ :  $100 \mu\text{g/L}$ ;  $\blacksquare$ :  $200 \mu\text{g/L}$

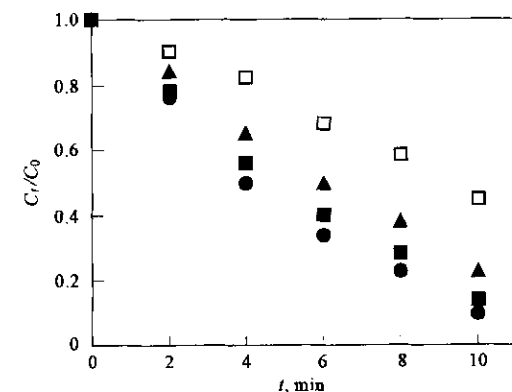


Fig. 7 Degradation of nitrobenzene during catalytic ozonation at different temperature

Conditions: pH 6.80; initial nitrobenzene concentration:  $50 \mu\text{g/L}$ ; total ozone applied:  $1.5 \text{ mg/L}$ ; number of ceramic honeycombs used: 5 blocks; background: distilled water; temperature:  $\square$ :  $10^\circ\text{C}$ ;  $\blacktriangle$ :  $20^\circ\text{C}$ ;  $\blacksquare$ :  $30^\circ\text{C}$ ;  $\bullet$ :  $40^\circ\text{C}$

ozone solubility, which decreases with the increase of temperature. When at lower temperature ranges, the increase of temperature yields the increase of the chemical reaction rate and the ozone self-decomposition rate. But the ozone

solubility decreases in water at higher temperature and at the same time the further oxidation of the intermediate compounds consumes more ozone, which causes negative effect on the degradation rate of nitrobenzene (from 20 to 40°C). In this ozonation system, the room temperature is among the optimal range considering the operational conditions.

### 2.5 Influence of pH value on the ozonation rate of nitrobenzene

The aqueous reaction between ozone and substances includes the direct reaction of molecular ozone and indirect reaction of OH radicals generated from ozone decomposition. It was reported that ozone decomposition in water is initiated by OH<sup>-</sup> and the rate of decomposition of ozone increases rapidly with the increase of pH value (Stachelin, 1982; Tomiyasu, 1985; Hoigné, 1997).

As observed in Fig. 8 and Fig. 9, the increase of pH value lead to a marked consumption of ozone in catalytic ozonation process, at the same time the highest extent of degradation for nitrobenzene was achieved in alkaline conditions. Additionally, this result is similar to that in 2.1, more ozone was consumed with higher catalysts dosages used, and the degradation of nitrobenzene improved. The removal rate of nitrobenzene at various catalyst dosages and pH values was directly proportional to the consumed ozone rate.

Based on the above results, it is reasonable to accept that both the increase of catalyst dosages and pH values accelerated ozone decomposition, more hydroxyl radicals were generated during the catalytic oxidation process. At neutral pH, the catalytic ozonation also presents a good potential to destroy nitrobenzene.

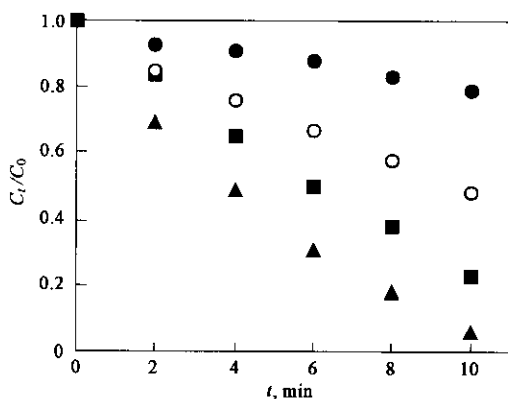


Fig. 8 Degradation of nitrobenzene during catalytic ozonation at different solution pH

Conditions: temp., 21 ± 1°C; initial nitrobenzene concentration: 50 µg/L; total ozone applied: 1.5 mg/L; number of ceramic honeycombs used: 5 blocks; background: distilled water; pH value: ●: pH = 3; ○: pH = 5; ■: pH = 7; ▲: pH = 9

### 2.6 Influence of *tert*-butanol on the ozonation rate of nitrobenzene

It is well known that *tert*-butanol is a stronger radical scavenger due to its higher reaction rate constant with hydroxyl radicals ( $K_{OH}^{Lz,rad.} = 5 \times 10^8 \text{ mol}/(\text{L} \cdot \text{s})$ , AWWA Research Foundation). *tert*-butanol reacts with hydroxyl radicals and generates inert intermediates, thus causing termination of the radical chain reaction. Therefore, it is a suitable indicator for radical type reaction because of its stronger scavenging effect on hydroxyl radicals.

Fig. 10 shows that the presence of *tert*-butanol (8 mg/L)

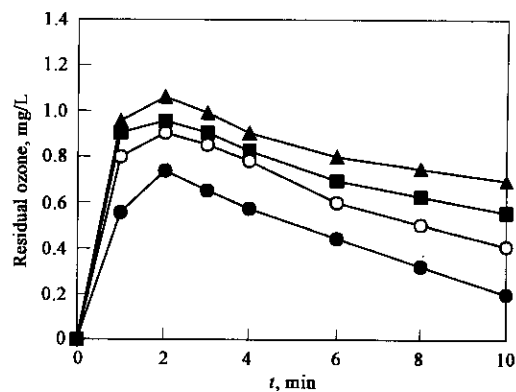


Fig. 9 Effect of pH values on residual ozone concentration in aqueous solution Conditions: temp., 21 ± 1°C; initial nitrobenzene concentration, 50 µg/L; total ozone applied: 1.5 mg/L; number of ceramic honeycombs used: 5 blocks; background: distilled water; pH value: ▲: pH = 3; ■: pH = 5; ○: pH = 7; ●: pH = 9

in the water results in a significant reduction of nitrobenzene removal during catalytic ozonation. It is seen in Fig. 10 that the corresponding residual ozone is not strongly influenced by addition of *tert*-butanol. In the case of ozone alone, *tert*-butanol also retarded the degradation of nitrobenzene, indicating that little, but measurable degradation of nitrobenzene by ozone alone, may be performed principally by a small extent radical formation generated by ozone decomposition rather than molecular ozone.

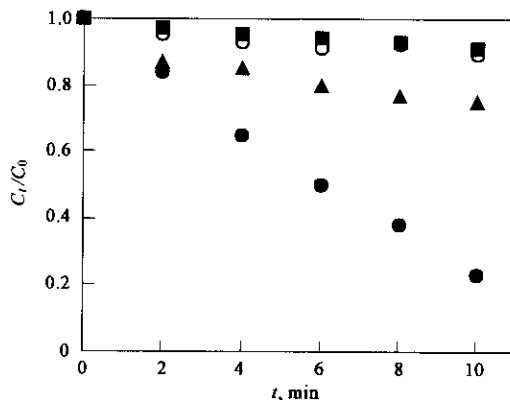


Fig. 10 Effect of *tert*-butanol on the degradation of nitrobenzene Conditions: temp. 21 ± 1°C; pH 6.80; initial nitrobenzene concentration: 50 µg/L; initial *tert*-butanol concentration 8 mg/L; total ozone applied: 1.5 mg/L; number of ceramic honeycombs used: 5 blocks; background: distilled water. ■: ozone alone with *tert*-butanol; ○: catalytic ozonation with *tert*-butanol; ▲: ozone alone without t-butanol; ●: catalytic ozonation without t-butanol

### 2.7 Influence of ceramic honeycombs on the ozonation rate of nitrobenzene after multiple-repeated use

The lifetime of ceramic honeycombs was investigated under the same operation conditions in present experiment. As shown in Fig. 11, there is no change of nitrobenzene removal in catalytic ozonation after ceramic honeycombs being continuously used (about 30 times). Compared to other catalysts used in catalytic ozonation reactions, ceramic honeycombs exhibited more chemical stability and much easier operation, especially there is not necessary to treat catalysts after water oxidation pretreatment. Therefore, it is believed that ceramic honeycombs are effectively and economically feasible to water treatment.

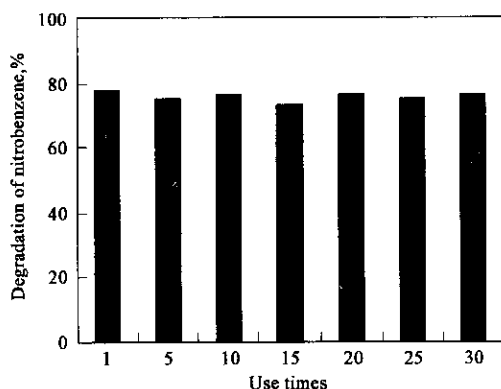


Fig. 11 Degradation of nitrobenzene in catalytic ozonation after ceramic honeycombs repeated use

Conditions: temp.,  $21 \pm 1^\circ\text{C}$ ; pH 6.80; initial nitrobenzene concentration:  $50 \mu\text{g/L}$ ; total ozone applied:  $1.5 \text{ mg/L}$ ; number of ceramic honeycombs used: 5 blocks; background: distilled water; reaction time: 10 min

## 2.8 Preliminary reaction mechanism

The reaction mechanisms of the heterogeneous catalytic ozonation are not uniform, because the applied catalysts ( $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{TiO}_2$  etc.) have different chemical characters, therefore, there are several explanations. Some papers recommended the adsorption process plays an important role, the proposed heterogeneous catalytic ozonation mechanism consists of organic molecules or dissolved ozone adsorbed on the catalyst surface during the reaction process or simultaneous adsorption of ozone and organic molecules on the catalyst surface (Cooper, 1999; Beltrán, 2002; Mathias, 2004). A majority of authors assume that hydroxyl radicals generated from ozone decomposition chain reaction were the dominant oxidation reagent, although the mode of initiation of the radical chain generating differs greatly (Ma, 1999; Mathias, 2004; Park, 2004). It is also considered that hydroxyl radicals are likely absent in some catalytic ozonation systems because the reaction is not influenced by the presence of radical scavenger such as bicarbonate and *tert*-butanol (Logemann, 1997; Beltrán, 2004).

In present experiment the degradation of nitrobenzene was obviously enhanced with ceramic honeycombs used in ozonation system. It is believed that hydroxyl radicals were produced in oxidation process, because with catalysts used the residual ozone in water was much lower than ozone alone and the degradation of nitrobenzene was strongly influenced by *tert*-butanol. To confirm the effect of  $\text{OH}^\cdot$  on oxidation reaction in the aqueous solution, EPR experiment was carried out. Nitrobenzene solution,  $\text{O}_3$  and the catalyst powder were mixed with DMPO dissolved in ultra-pure water. Immediately

after the mixing,  $25 \mu\text{l}$  of the sample solution was transferred into a capillary tube, and EPR spectra were recorded in the X-band on a Bruker ESP spectrometer at room temperature. As shown in Fig. 12, a much stronger signal of  $\text{OH}^\cdot$ , which had the typical spectrum of 1:2:2:1, was presented in catalytic ozonation than ozonation alone process. This indicated that more  $\text{OH}^\cdot$  was surely produced with ceramic honeycombs used in ozonation process.

Fig. 3 and Fig. 9 illustrate that the decomposition of ozone is directly proportional to the ceramic honeycomb dosages and pH values. The ozone decomposition occurs both on the surface of catalysts (including the liquid-solid interface) and in the bulk solution, with the increase of catalyst dosages the decomposition rate of ozone is significantly enhanced. This phenomenon indicates that the decomposition rate on the catalysts surface is higher than in the bulk solution, because the pH at the liquid-solid interface may be higher than in the bulk solution. Correspondingly, the oxidation rate of nitrobenzene may be enhanced at the liquid-solid interface because the high concentration of both hydroxyl radicals and nitrobenzene existed.

Based on these results, it can be concluded that nitrobenzene removal via catalytic ozonation occurs at two locations: (1) on the surface of catalysts involving the liquid-solid interface; (2) in the bulk solution. Fig. 2 shows that nitrobenzene removal was very limited in the case of ozonation alone (in bulk reaction), therefore, the reaction in bulk seems not dominant to the degradation rate.

As schematized in Fig. 13, it is assumed that the dissolved ozone adsorbs first and then decomposes rapidly due to the presence of hydroxyl ions on the surface of catalysts. The reaction of the hydroxyl ion with ozone produces one superoxide anion radical ( $\text{O}_2^{\cdot-}$ ) and one hydroperoxyl radical ( $\text{HO}_2^\cdot$ ), the radicals subsequently reacts quickly with another  $\text{O}_3$  produced the ozonide anion radical ( $\text{O}_3^{\cdot-}$  or  $\text{HO}_3^\cdot$ ), hydroxyl radicals  $\text{OH}^\cdot$  generated from the ozonide radicals decomposition. According to this suggestion, adsorption of nitrobenzene onto catalyst surface can be accepted as one of the steps of the catalytic ozonation mechanism, but not the key process because the nitrobenzene adsorption in Fig. 2 was not obvious.

## 3 Conclusions

The use of cordierite honeycombs for the ozonation of nitrobenzene in water significantly improved its degradation compared to the case of non-catalytic ozonation. The decomposition rate of ozone in solution is strongly pH-

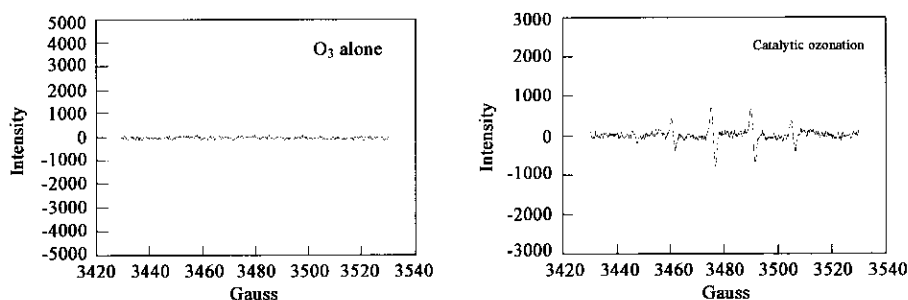


Fig. 12 Comparison of the intensity of DMPO- $\text{OH}$  adduct signals with catalysts existed and ozonation alone DMPO and  $\text{O}_3$  concentration are 80 and  $0.125 \text{ mmol/L}$ , respectively

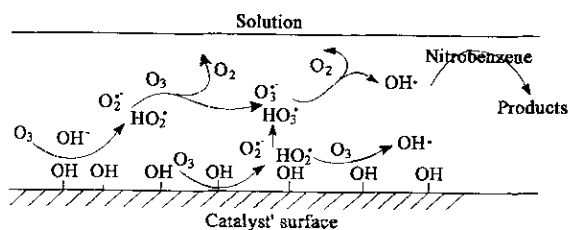


Fig. 13 Suggested reaction mechanism during catalytic ozonation

dependent, attributed to the initiation of chain reaction between ozone and hydroxyl ions. Variables such as catalyst dosages, temperature, initial concentration of nitrobenzene and applied ozone dosages play positive influence on the nitrobenzene removal. With the addition of *tert*-butanol the degradation rate of nitrobenzene decreased sharply. EPR experiments confirmed that with the catalyst was applied larger amount of  $\text{OH}^\cdot$  radicals generated probably by hydroxyl ion and ozone molecule in vicinity of catalysts' surface.

The obtained results suggest that ceramic honeycombs be of higher catalytic activity and longer lifetime in catalytic ozonation. Compared to other heterogeneous catalytic oxidation processes the present catalytic ozonation of nitrobenzene highlights the merits and potential applications of ceramic honeycombs in large-scale water treatment systems. Further research on the influence between the morphology of ceramic honeycombs and the oxidation mechanism is still in progress.

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