Water Ozonation with Copper Catalyst for Organic Pollutants Removal

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Abstract
This work presents high-porous honeycomb copper catalyst for organic pollutants removal from water during the ozonation process. This catalyst demonstrates high efficiency in removing target compounds (oxalic and benzoic acids and methylene blue), appropriate stability and resistance to abrasion. Copper catalyst behavior in the ozonation process was investigated. It was found that under ozonation conditions reversible oxidation/reduction of the copper surface layer takes place. In contact with ozone, copper surface can easily be oxidized resulting in formation of copper oxides. As expected, it leads to decomposition of organic substances during ozonation and reduction of copper catalyst surface layer. Copper (II) oxide was also found to be an active catalyst in oxidation of organic pollutants with ozone, but it is not appropriate to use bulk CuO because of its low abrasion resistance. Copper (II) ions that form due to dissolution of catalyst surface layer with participation of the acidic medium in the ozonation process were detected. Pollutants removal efficiency at different pH values was also studied. It was found that catalytic removal of organic pollutants takes place at low pH, as compared to low efficiency of hydroxyl-radical formation at the acidic pH. A possible scheme for organic pollutants removal during ozonation with copper catalyst was proposed.

Introduction
Since ozone has long been used as an oxidizing agent for water purification, it is well known that it is an environmentally safe oxidant which has the ability to decompose organic pollutants, decrease water colorization, and remove manganese and iron ions. It also has strong disinfection properties and the ability to improve water taste and odour [1]. However, ozone oxidation of organic substances often leads to formation of stable organic by-products (carboxylic acids, aldehydes, etc.). Therefore, top priority is given to creation of advanced pollutants oxidation techniques that use homogeneous or heterogeneous catalysts to improve completeness of organic substances decomposition and to increase effectiveness and economic efficiency.

Various metal oxides (e.g. Fe₂O₃ [2], Co₃O₄ [3], TiO₂ [4], NiO [4], ZnO [5], MnO₂ [6], CuO [4, 7], Al₂O₃ [8], CeO₂ [9]) without support, metals and metal oxides with oxide supports (e.g. CuO/Al₂O₃ [10], Fe₂O₃/Al₂O₃ [11], TiO₂/Al₂O₃ [12], Ru/CeO₂ [13], Ru/Al₂O₃ [14]), oxides on other supports (e.g. zeolites [15], silica gels [16], GAC [17]) are used as catalysts in such processes. Also some carbon materials [18-20], different types of natural matters (e.g. pumice [21], brucite [22], bauxite [23], zeolite [24-26], volcanic sands [27]) and other materials (e.g. perfluorooctyl alumina (PFOAL) [28], metal-doped carbon aerogels [29], modified ceramic honeycomb [30]) demonstrate high catalytic activity for organic pollutants decomposition in water with ozone. Technologically, the main obstacle for extensive application of heterogeneous powder and granular catalysts is their low resistance to abrasion. This fact caused the necessity to add the filtration stage that makes the water purification process more complicated and
expensive. Thus, using catalysts of another type – massive, metal containing, resistant to abrasion – is more promising. This paper studies the activity of the massive copper catalyst – high-porous honeycomb copper – in organic pollutants decomposition in water during ozonation.

Phenols, carboxylic acids, alcohols, etc. are used as model compounds in studies on catalytic ozonation. Oxalic and benzoic acids, methylene blue were chosen for the present work. Oxalic acid is the product of aromatic organics ozonation and its reaction with ozone is slow. Benzoic acid is used as a model compound for the ozonation of aromatics. Methylene blue is commonly used as a dye which has a complicated molecular structure and contains heteroatoms.

**Experimental**

Catalyst samples were prepared by the method described in [31]. High-porous honeycomb copper catalyst obtained has specific surface area of 5 m²/g and 98% porosity. The porosity was measured by volumetric method, and the specific surface area was determined by the BET method using TriStar 3020 Surface Area Analyzer (Micromeritics, USA). The catalyst surface morphology and composition were investigated via Philips SEM 515 Scanning Electron Microscope (SEM and EDX-analysis).

To study organic pollutants decomposition in the ozonation process, the reactor, in simultaneous contact with liquid, solid and gaseous phases, was used. Ozonation was carried out in glass vessel. Model solution was placed in it, and catalyst particles (cubic shape, about 10×10 mm) were suspended in the solution. Gas was fed through a glass filter (40 mesh) in the bottom of the vessel. Stirring was implemented by gas feeding. Ozone was fed as ozone-air mixture from “Polikor-V” ozonizer. The initial gas for ozone obtaining was air fed to the ozonizer by the air compressor.

As a rule, the experimental conditions were the following: treated solution volume – 100 mL, 1 L; pollutant initial concentration – from 8·10⁻⁴ to 0.01 M; gas flow rate – 1,000 mL/min; ozone concentration in the liquid phase (measured in accordance with GOST 24683-81) – 0.03 mg/mL; ozonation period – up to 60 min; pH – non-adjustable or adjustable (pH 2 – HClO₄, pH 9 – Na₂B₄O₇·10H₂O); temperature – 20 °C. The catalyst mass varied from 0.2 to 2.5 g; CuO obtained via catalyst thermal air oxidation (500 °C) and CuSO₄ (chemically pure) serving as source of copper ions were used.

Model organic compounds concentration was measured as total organic carbon concentration (TOC-VCPN Total Organic Carbon Analyzer, Shimadzu), chromatography was also used for experiments with benzoic acid (Spectra SYSTEM, RESTEK column, C-18, 0.03 M phosphoric acid addition, flow rate 1 mL/min, wavelength 240 nm). The accuracy of removal rate determination is 1%.

Pollutants removal was calculated by equation:

\[
100 - \left( \frac{C_M}{C_I} \right) \times 100 = \text{removal, } \%
\]

\(C_M\) – measured current concentration, \(C_I\) – initial concentration.

Copper ions concentration in the solution was determined via atomic absorption spectroscopy (SOLAFR S2 Atomic Absorption Spectrophotometer, USA), the accuracy is 2%. The catalyst surface composition was also studied via FTIR (Nicolet 6700 IR Spectrometer) and UV-Vis diffuse-reflectance spectroscopy (Evolution 600).

**Results and discussion**

**Benzoic acid and methylene blue removal**

According to the results of chromatographic analysis (Fig. 1), benzoic acid concentration decreases similarly in the ozonation process with and without the catalyst. However, total organic carbon concentrations are different for these two cases (Fig. 2). It can be explained by the fact that benzoic acid decomposes alone resulting in formation of stable organic by-products during ozonation.

![Fig. 1. Benzoic acid removal: (1) catalytic experiment; (2) ozonation alone. Pollutant concentration was measured by chromatography. Benzoic acid initial concentration – 8·10⁻⁴ M, catalyst mass – 0.5 g, solution treated volume – 1 L.](image-url)
Thereby, ozonation alone provides 32% of total organics removal, at the same time catalytic ozonation leads to 60-65% of total organics decomposition.

In the case of methylene blue ozonation, ~100% dye decomposition is achieved after 1 and 5 minutes of treatment for catalytic and non-catalytic experiments correspondingly.

**Oxalic acid removal, catalyst stability**

Figure 3 represents data on oxalic acid removal by ozonation. It can be seen that during catalytic ozonation pollutant removal increases significantly. After 60 minutes of ozonation with the copper catalyst about 70% of oxalic acid was decomposed.

The data on the copper catalyst stability in oxalic acid ozonation process is represented in Table 1 (small amount of the catalyst was used for convenience of the analysis). It demonstrates that the catalyst maintains its activity within at least 20 ozonation sessions.

**Table 1**

| Procedure                  | Ozonation alone | 1st catalytic ozonation | 5th catalytic ozonation | 20th catalytic ozonation |
|----------------------------|-----------------|-------------------------|-------------------------|--------------------------|
| OA removal, %              | 7               | 21                      | 18                      | 17                       |

**Copper catalyst behavior in the ozonation process**

The role of the catalyst in the ozonation process was studied using oxalic acid as a model pollutant. It was found that oxalic acid sorption doesn’t occur on the copper catalyst surface (FTIR-spectroscopy, Fig. 4 for high-porous honeycomb copper catalyst and copper oxide [32, 33, 34]). Thus, pollutant removal isn’t caused by its sorption.

Fig. 4. FTIR-spectra of high-porous honeycomb copper before (1) and after (2) contact with 0.1 M oxalic acid solution. There are not additional peaks of OA species on the catalyst surface. And for comparison FTIR-spectra of CuO before (3) and after (4) contact with 0.1 M oxalic acid solution (intensive peak at 1314 cm\(^{-1}\) is assigned to \(\nu_{as}(C-O)\) for oxalate adsorbed in outer-sphere mode [22], peak at 1361 cm\(^{-1}\) is typical for valence vibration of acidic group C-O [23] and peak at 1711 cm\(^{-1}\) relates to \(\nu_{as}(CO_2)\) in surface-adsorbed oxalate complex [24]).

It is well-known that under high pH values the process of ozone decomposition is faster, which
causes the chain reaction of forming hydroxyl-radiicals. OH-radicals are able to oxidize organics fast and unselectively.

Several authors point out that the main purpose of catalysts application is production of these radicals in a neutral and alkaline medium. However, this process is slow in acidic solutions.

Figure 5 represents the data on oxalic acid removal on the copper catalyst at pH 2 and 9. Pollutant removal rate is higher at pH 9, but the process doesn’t stop at the acidic pH. Possibly, in the acidic medium the oxalic acid removal proceeds not due to OH-radicals formation but through another mechanism.

Figure 6 shows the data on changes in oxalic acid concentration depending on the amount of the catalyst (in terms of surface area). These data corresponds with [35, 36] and point out that the catalyst surface takes part in oxalic acid ozonation process. Besides, the experiment of putting out the catalyst during ozonation was carried out. The results are represented in Fig. 7. The fact that the catalyst exclusion from the system doesn’t result in decreased subsequent oxalic acid concentration indicates that the process is more likely to have heterogeneous nature.

The copper catalyst surface structure before and after its participation in the ozonation process was investigated [37]. Figures 8-10 show SEM-data for freshly prepared catalyst surface and for that after catalysis experiments. It was figured out that after participating in ozonation process a defective layer is formed on the copper catalyst surface. This layer is easily oxidized by air oxygen resulting in formation of copper oxides (EDX-data). After vacuum drying, the surface of the catalyst used in the ozonation process doesn’t demonstrate structural and composition changes.
Its depth and oxidation products composition depend on oxalic acid concentration in the solution. It can be explained by the contact between the catalyst surface and ozone during the ozonation process. The availability of copper oxides causes the need to consider copper oxides contribution to the whole process.

There are several processes that can take place on the copper catalyst surface containing copper oxides:

1. Interaction with ozone and the chainreaction of its decomposition, which leads to formation of hydroxyl-radicals.
2. Surface oxides dissolution resulting in the formation of hydrated copper species (depending on pH), including copper oxalates.
3. Oxalic acid anions sorption that can be caused by positive surface charge (pHpc for CuO and Cu2O are higher than 0.001 M oxalic acid solution at pH~3). All these processes should be taken into account in the copper catalyst behavior investigation.

In order to compare the metallic copper honeycomb catalyst and the bulk copper (II) oxide catalytic activity, an experiment involving these two materials was carried out (CuO was prepared via thermal oxidation of the copper honeycomb catalyst – via calcination in the air at the temperature of 500ºC). Moreover, bulk CuO sorption ability to oxalic acid was also investigated. At low pH values, copper oxides surface layer is likely to dissolve forming copper ions. Therefore, in addition to oxalic acid concentration measurement, copper ions concentration was also determined. The results obtained are presented in Table 2.

| Table 2 |
| Copper (II) oxide and metallic copper catalytic activity comparison (experiment duration – 20 minutes, oxalic acid initial concentration – 0.001 M, solution treated volume – 0.1 L) |
| Catalyst | Catalyst mass, g | Process | OA removal, % | OA removed, mol | Cu²⁺ content, mol |
|-----------|-----------------|---------|----------------|----------------|------------------|
| Metallic copper | 0.4 | Sorption | 3 | 3.0·10⁻⁶ | 3.8·10⁻⁶ |
| | | Ozonation | 39 | 3.3·10⁻⁴ | 6.9·10⁻⁵ |
| Bulk CuO | 0.4 | Sorption | 17 | 1.6·10⁻⁴ | 4.0·10⁻⁵ |
| | | Ozonation | 71 | 4.9·10⁻⁴ | 3.7·10⁻⁵ |
As it can be seen, CuO sorption ability and pollutant removal rate during ozonation are higher than that of the copper honeycomb catalyst. Possibly, copper (II) oxide has higher catalytic activity due to its high sorption ability. It was found that CuO mechanical stability is not high enough – during the ozonation process it abraded and crushed. This fact can also cause the increase in CuO catalytic activity because of the enlargement of the catalyst specific surface area. Such low bulk CuO mechanical stability makes this material inappropriate for the water ozonation process.

The amount of copper ions detected in the solution after ozonation is equal to the amount of oxalic acid removed from it (Table 2). Therefore, it can be suggested that pollutant removal is caused not by a heterogeneous mechanism but through another way. Copper (II) ions with oxalic acid can form slightly soluble copper oxalates, complexes, or Cu

\[\text{Cu}^{2+}\] can act as a catalyst for pollutant decomposition. To recognize the contribution of copper ions to the whole process, the experiment involving copper sulfate was carried out. The results are represented in Fig. 11.

![Fig. 11. Oxalic acid ozonation removal depending on copper (II) ions concentration in the solution.](a) whole graph; (b) its initial part. Oxalic acid initial concentration – 0.001 M, solution treated volume – 0.1 L, ozonation time – 20 minutes.

It is clear that increase in Cu

\[\text{Cu}^{2+}\] concentration leads to enhanced pollutant removal process. According to the dependence obtained, in the presence of 6.9 \(10^{-5}\) M copper (II) ions (this amount was detected in the solution after ozonation with the copper catalyst – Table 2) only 7\% of oxalic acid can be removed. But in fact 40\% removal takes place. In case of ozonation with CuO, 3.7 \(10^{-4}\) M of copper ions were found in the solution. According to Fig. 10, it should lead to 35\% oxalic acid removal. The actual removal rate is 71\%. On this base it can be concluded that homogeneous catalysis with copper ions is not the main mechanism of the process.

A possible scheme for the investigated process was proposed (Fig. 12). The oxalic acid decomposition in water on the copper catalyst with ozone consists schematically of two parts. One of them is prevailing in the alkaline medium (pH>7), and another one – in the acidic pH (pH<7). It should be emphasized that both of them can proceed simultaneously, but their contribution depends on the pH value.

![Fig. 12. A possible scheme of water organic pollutants decomposition by ozone on copper catalyst.](R – organic pollutant, oxalic acid in this case.)
In the alkaline pH, according to other authors [38, 39], OH-radicals formed during ozone decomposition play the main part in pollutant destruction. But we suppose that at low pH organics oxidation is based on interaction with the catalyst surface. Consecutive oxidation-reduction of the copper catalyst surface layer occurs, which causes pollutant oxidizing. Possible copper ions contribution as a homogeneous catalyst is also taken into account.

**Conclusion**

It was found that high-porous honeycomb copper catalyst has high activity in removing organic pollutants (oxalic and benzoic acids and methylene blue were used as target pollutants) from water during ozonation. Catalyst behavior in the ozonation process was investigated. It was figured out that the catalyst surface plays an important role in the whole process. The copper surface layer can dissolve resulting in the formation of copper (II) ions that are able to catalyze the pollutant removal homogeneously. Copper (II) oxide was also found to act as a catalyst, but it is not appropriate to use it because of its low abrasion resistance. On the basis of the results obtained, a possible scheme for organic pollutants removal during ozonation with copper catalyst was proposed.

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