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## **Catalytic oxidation of aromatic compounds by nanostructured ruthenium dioxide**

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Physico-chemical processes that can be used to free industrial leaks from contamination with aromatic compounds were considered in this work. It has been demonstrated that catalytic oxidation with ruthenium dioxide can serve as an effective purification method. An original way of detection of the catalytic oxidation process completion by the photoluminescent method is proposed. A block diagram of the purification setup is given. The results can be used to solve the problem of protecting the environment from certain harmful pollutants.

**Keywords:** catalytic oxidation, porous silicate glass, photoluminescence, environmental protection.

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### **Introduction**

Dispersion of semiconductor compounds to the level of an ensemble of nanoparticles significantly increases their effective surface. This leads to the enhancement of the luminescence of metal oxides [1-2], as well as a number of diatomic semiconductors [3-5], which expands the possibilities of their application in optoelectronics and luminescent sensors. At the same time, the oxides of some metals do not luminesce at all due to the peculiarities of their atomic structure. This statement applies, first of all, to metals of the platinum group, which have two incomplete electron shells with unequal principal quantum numbers, but close ionization energies [6]. Such substances can cause a redistribution of the intramolecular charge in chemically stable compounds, and therefore, stimulate some reactions that require catalysis. The catalytic properties of the materials are also surface phenomena [7], so the transformation into an ensemble of nanoparticles strengthens these properties. It is clear that such systems are not used in optoelectronics, however, they can be quite useful for creating other micro- and nanoelectronics devices, in particular, sensors of various functional purposes, as well as in systems for environmentally polluting leaks neutralizing.

### **I. Research and discussion**

It is known that the main components of most industrial emissions are aromatic compounds, namely, phenols and their derivatives. Phenols have very significant disinfecting properties, and at the same time they are well soluble in water, therefore, they easily spread in the environment, having a detrimental effect on flora and fauna. Both tautomeric forms of hydroquinones, which are derivatives of phenol, are also well soluble in water and, due to their toxicity, are also dangerous environmental pollutants. However, the oxides of these substances are practically insoluble in water. Therefore, the conversion of phenol into hydroquinones with the catalytic oxidation of the latter will make it possible to rid the leaks of aromatic pollutants by conventional settling. These reactions are possible when interacting with oxygen contained in the air [7], however, due to the chemical stability of benzene rings, such reactions are possible only under the condition of redistribution of the charge density inside the ring. Therefore, the problem of pollution from aromatic compounds remains unsolved.

We propose to use an ensemble of nanoparticles of the appropriate catalyst, which will stimulate the specified

redistribution. Ruthenium is the most suitable for this role [8]. Since ruthenium is a metal, it is hardly possible to saturate any porous matrix with it, but there is no special need for this. The point of interest here is not ruthenium as a metal, but only its atoms contained in a certain underoxidized compound (like dioxide), which could be deposited on the substrate with different methods, like chemical oxidation, ALD, MOCVD and other [9]. It must be unoxidized to preserve the atomic structure of ruthenium with two incomplete shells. Therefore, by saturating the matrix with soluble ruthenium trichloride followed by processing in the correct thermodynamic mode, it is possible to turn it into insoluble RuO<sub>2</sub> nanoparticles directly inside the pores. In this oxide, ruthenium atoms retain two incomplete electron shells, so such a system can be used for catalytic oxidation of aromatic compounds.

The specified system would work best if the substrate matrix is chosen correctly, because the substrate is an integral part of the formed ensemble of nanoparticles. Since the system will be placed in a fluid flow, there should be a high adhesion of the nanoparticles to the walls of the matrix to minimize their washout, which would lead to catalyst depletion. Our previous studies [10] have shown that the best adhesion occurs when a porous silicate glass with residual silica gel inside the pores is used as a matrix. This glass, moreover, is chemically inactive and mechanically quite durable, which ensures the reliability of the system.

It is important to fix the completion of the process in time during the catalytic oxidation: early-stage termination of the reaction will lead to incomplete neutralization of the pollutant, and late termination of the process will lead to unproductive use of the catalyst and its faster depletion. It is impossible to be sure about the end of the catalytic oxidation process in advance, because this process depends on many factors. First of all, it is the concentration of aromatic compounds and the density of their distribution in the solution. In addition, it is the volume of the reactor chamber and the number of matrices with ensembles of catalyst nanoparticles in them. The distribution of nanoparticles within the matrix is random. Taking this into account, some authors [11] advise using fairly expensive equipment to count oxidized and non-oxidized particles in the solution.

However, the use of such equipment for fixing the end of the catalysis process is not mandatory, if we take into account the peculiarities of the structure of phenol molecules and their oxides. The structure of a phenol molecule can be imagined as a hydrazone fragment with a hydroxyl substituent of a dye based on a 4-valent state [12], in which the role of a coordination node is played by a hydrogen atom. In the same way, the molecules of both tautomeric forms of hydroquinone can be imagined as dyes of the same type, in which the role of the coordination node is played by the hydroxyl group. Our previous luminescence studies of dyes of the specified type [13] showed that with hydroxyl substitution in the hydrazone fragment, the most intense luminescence occurs due to radiative transitions between electron-vibrational sublevels of the system, and is almost independent of the structure of the coordination node, but depends on tautomeric form.

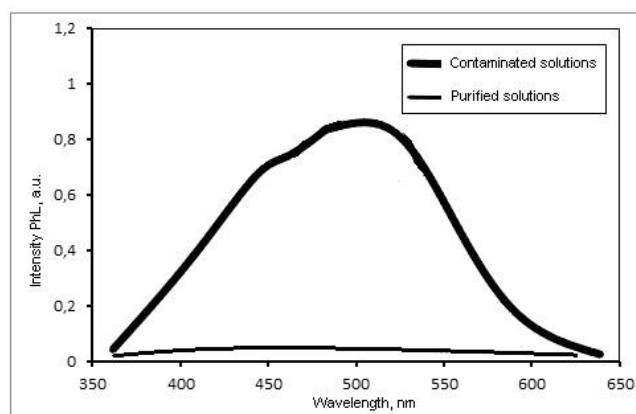
Phenol does not have tautomeric forms and, at the first stage of catalytic oxidation, it turns into one of the tautomeric forms of hydroquinone first, and later both tautomeric forms of hydroquinone lose hydrogen from hydroxyl groups and the ordinary oxygen substituents appear in their place, which indicates the end of the oxidation process. These substituents are connected to the benzene ring by a permanent double bond. Such systems do not contain electronic vibrational sublevels, therefore, they practically do not luminesce. Let's pay attention to the fact that RuO<sub>2</sub> nanoparticles are also not luminescent, so they do not add any contribution to the spectrum.

Thus, by observing the luminescence of the solution in the reactor chamber with the help of a standard fluorescent device, it is possible to claim the end of the oxidation process when the mentioned luminescence disappears.

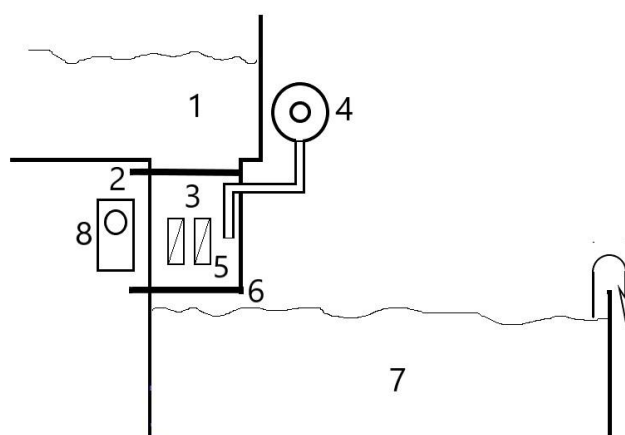
The luminescent setup consisted of a quartz monochromator SF-4, a photoelectronic multiplier FEU-69, which had a sensitivity in the range of 280-850 nm and played the role of a photodetector, and a selective amplifier for synchronization with the frequency of the excitation laser. An ultraviolet LCS-DTL-374QT laser with a wavelength of 335 nm and a power of 1.5 mW was used to excite photoluminescence spectra. The measurement data were transmitted by the USB-oscillography program to the computer monitor with the help of an analog-digital converter [14].

In Fig. 1. typical photoluminescence spectra of a solution of aromatic compounds are shown. A rather wide spectrum of the mixture of phenol and two tautomeric forms of hydroquinone in the process of catalytic oxidation changes all the time due to the transformation of phenol randomly into one or another form of hydroquinone. The contribution to the final spectrum of each of the specified substances is also random, since the transformation of phenol into hydroquinone cannot be regulated, therefore it is impractical to separate the corresponding spectra in each specific period of time, because since the main purpose of described research on the catalytic oxidation of aromatic compounds for the purpose of cleaning industrial leaks, the specified features of the luminescence spectra of hydroquinone in our case are not significant. It should be noted that the photoluminescence intensity of the system is constantly decreasing, because all the aromatic compounds contained in the flow are gradually transformed into luminescent inactive oxides during the process of oxidation. Finally, the luminescence disappears, as can be seen from Fig. 1, and this is the signal of the catalytic oxidation reaction completion.

Based on the research results, it is possible to propose a setup built according to the scheme shown in Fig. 2. Industrial solutions contaminated with aromatic compounds could be accumulate in a tank of certain sizes (1). Since the catalytic oxidation reaction can be effectively carried out in a limited volume, the specified tank should be connected with a nozzle to the reactor chamber (3), in which a certain number of porous plates with ensembles of RuO<sub>2</sub> catalyst nanoparticles (5) are installed, and separated from it by a suitable barrier (2). Pushing it away, in order to clean the contaminated leaks, a certain part of them is placed in the reactor chamber (3),



**Fig. 1.** Typical photoluminescence spectra of solutions contaminated with aromatic compounds and purified from them.



**Fig. 2.** Structural diagram of a treatment setup for aromatic pollution removal from industrial sources. 1 – a reservoir with polluted water; 2- entrance plug into the reactor chamber; 3 – reactor chamber; 4 – compressor for enriching the reactor chamber with oxygen; 5 – matrices with catalyst nanoparticles; 6 – outlet plug from the reactor chamber; 7 – reservoir-settlement of hydroquinone oxides; 8 – fluorescence measurements setup.

where catalytic oxidation takes place. At the same time, the plug (2) is closed and oxidation occurs due to oxygen from the air [15], which is enriched in the reactor chamber with the help of a compressor unit (4). After the end of the reaction, which is fixed by photoluminescence spectra (Fig. 1.) with the help of a luminescent device (8), purified water with a mixture of hydroquinone oxides is poured into the sedimentation tank (7) by moving the output plug (6). After complete precipitation of hydroquinone oxides, clean water is drained from the sump by gravity or with the help of special pumps and is completely suitable for reuse.

## Conclusions

Oxides of aromatic substances, unlike the substances themselves, are not soluble in water, therefore, do not pollute the environment. However, they have a different, less energetically favorable charge density distribution in the molecule than the substances themselves, due to which

the oxidation process must be catalytic.

As a catalyst, it is advisable to use ruthenium dioxide, which helps redistribute the charge in the molecule of the pollutant, but for the effectiveness of catalysis, it should have a maximally large surface. The best way to develop the surface of the catalyst is to transform it into the form of an ensemble of nanoparticles in a suitable matrix, which could be a porous silicate glass with residual silica gel inside the pores.

The end of the catalytic oxidation process can be effectively recorded by the photoluminescence method when the luminescence excitation of the system disappears.

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## Каталітичне окислення ароматичних сполук наноструктурованим діоксидом рутенію

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Розглянуто фізико-хімічні процеси, які можуть бути використаними для звільнення промислових витоків від забруднення ароматичними сполуками. Продемонстровано, що ефективним способом очищення може бути каталітичне окислення діоксидом рутенію. Запропоновано оригінальний спосіб фіксування завершення процесу каталітичного окислення фотолюмінесцентним методом. Наведено блок-схему очисної споруди. Результати можуть бути використаними для розв'язання проблеми захисту довкілля від певних шкідливих забруднювачів.

**Ключові слова:** каталітичне окислення, шпаристе силікатне скло, фотолюмінесценція, очисні споруди, захист довкілля.