

# Catalysis of Wastewater Pollutants by Ruthenium Nanooxide in Porous Glass



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## Introduction

Phenol is one of the main wastewater pollutants in industry and in everyday life. Wastewater purification is usually done by catalytic oxidation, which makes it possible the transition to closed waste-free technologies.

The possibility of using ensembles of ruthenium nanooxide in porous glass for the catalysis of phenol in wastewater is considered in the paper.

## The formulation of the problem

Phenol is highly soluble in water and therefore is a persistent environmental pollutant. It is difficultly oxidized, as this would lead to the formation of energetically extremely disadvantageous dangling bonds. A phenol derivative, hydroquinone, upon oxidation forms water-insoluble oxides without dangling bonds. Consequently, the conversion of phenol to hydroquinone followed by oxidation and precipitation of the oxide is one of the simplest ways to remove phenol from wastewater. Hydroquinone has two tautomeric forms: hydroquinone-2, the oxide of which is schematically shown in Fig. 1, 3), and hydroquinone-4, (Fig. 1, 4). The unequal distribution of the electron charge density in both oxides differs significantly from the uniform charge distribution in benzene or phenol.

Thus, in order to carry out the transition of phenol to hydroquinone with subsequent oxidation, it is necessary to change significantly the electronic configuration inside the benzene ring, which requires catalytic oxidation. The role of a catalyst can be played by a metal with two uncompleted electron shells, the upper one of which is s. The capture of an electron to complete the upper shell in this case will be energetically unfavorable, since in this case the lower shell will remain incomplete and the metal will tend to return the captured electron.

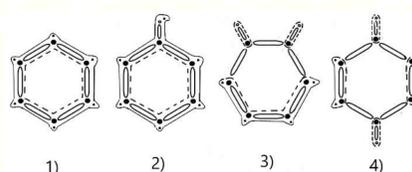


Fig. 1. Schematic distribution of the electron charge density in benzene (1), phenol (2), hydroquinone-2 oxide (3) and hydroquinone-4 oxide (4).

Large black circles represent carbon, small ones - hydrogen, medium white - oxygen. Solid thick lines indicate the region of propagation of  $sp^2$  and  $sp^3$  bonds, thin solid  $sp^2$  bonds and dashed  $p\pi$  bonds.

Thus, the catalytic properties are associated with the contradiction between the Pauli principle and the principle of minimum total energy of the system. Platinum group metals have such properties, and the cheapest of them is ruthenium with an external electronic configuration of  $4d^75s^1$ . Since the surface atoms will participate most actively in the catalytic process, in order to increase the efficiency of the reaction, the maximum development of the surface should be achieved. Aiming this, it is advisable to transform ruthenium into an ensemble of nanoparticles within a suitable matrix.

## The Choice of Matrix

Requirements for matrix for the formation of an ensemble of nanoparticles:

mechanical strength;

chemical inertness;

high adhesion of the catalyst to the walls of the matrix to prevent its washout.

Thus, as a matrix for the formation of an ensemble of  $RuO_2$  nanoparticles, porous silicate glass can be used, which is sufficiently strong mechanically and chemically inert.

Depending on the technological features of the formation, 4 types of porous silicate glass A, B, C and D are usually considered. An electron microscopic image of their structure is shown in Fig. 2. The types of glass differ in pores sizes and in the presence or absence of secondary silica in them. Glasses of type A and B are fine-pored, while glasses C and D are large-pore. Glasses of type A and C contain secondary silica in their pores. Glasses of type B are depleted of them, and in glasses of type D it is practically absent. The silica particles in Figure 2 are visible as white spots.

The use of finely porous silicate glass with residual silica gel inside the pores (type A) differs significantly for the better both from the use of organosilicate rods and other types of glass. Such a good result is explained, on one hand, by the rather small size of the nanoparticles of the ensemble (less than 20 nm due to the limitation by the predominant pore size) and, on the other hand, by the separation properties of silica gel, preventing the aggregation of the forming nanoparticles, which additionally increases the efficiency of catalysis.

## Luminescent studies

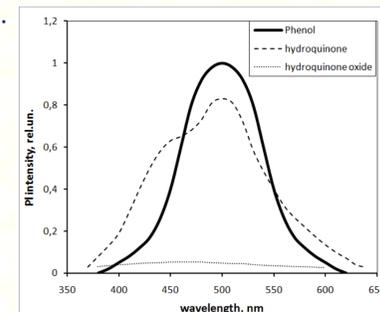
The phenol molecule can be represented as a hydrazone fragment with a hydroxyl substituent of a tetravalent tin-based dye molecule. In this case, the hydrogen atom will simply play the role of the coordination node. Our previous luminescence studies of dyes of this type showed that, upon hydroxyl substitution, the intensity of their luminescence arising from transitions between the electronic-vibrational sublevels of the system weakly depends on the nature of the coordination site, but may depend on the tautomeric form. Phenol-tautomeric forms are absent, and therefore the spectrum of its photoluminescence has a Gaussian-like shape with one peak, Fig. 4.

In the oxidation process, phenol is first converted into hydroquinone, the presence of which in wastewater is also harmful to the environment. Like phenol, its molecule can also be represented as a hydrazone fragment with a hydroxyl substituent of a tetravalent tin-based dye molecule. But the second hydroxyl group will play the role of a coordination site for it. In this case, two tautomeric forms are possible: 2 and 4.

During oxidation, they will arise randomly and it is impossible to separate them. By analogy with dyes, tautomeric form 4 glows approximately one and a half times less intensively than tautomeric form 2 and its luminescence peak is slightly shifted towards

short waves side. The both tautomeric forms will contribute to the total luminescence spectrum, and therefore it looks somewhat more diffuse in comparison with phenol, with a slightly lower intensity, greater width, and with two peaks clearly distinguished in it, corresponding to two tautomeric forms, Fig. 4.

Fig. 4. Photoluminescence spectra of phenol, hydroquinone and its oxides.



It should be noted that the areas under the curve for the spectra of phenol and hydroquinone coincide, which indicates the same number of molecules in both systems.

## Conclusion

The use of ruthenium dioxide as a catalyst for the purification of waste water from phenol is one of the most preferred methods of purification. Moreover, the formation of this catalyst in the form of ensembles of nanoparticles in the matrix of porous silicate glass of type A prevents its washout during the cleaning process. The indicator of the end of the oxidation process of phenol and its derivative, hydroquinone, is indicated by the termination of the luminescence of the catalytic system.

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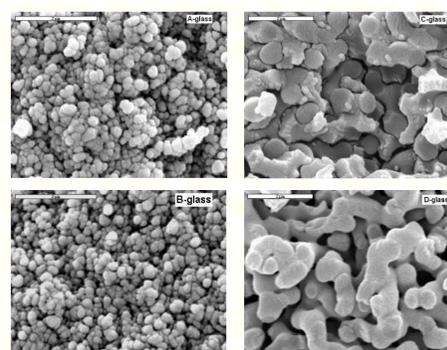


Fig. 2. Electron microscopic images of four types of silicate porous glass A, B, C and D [ ]

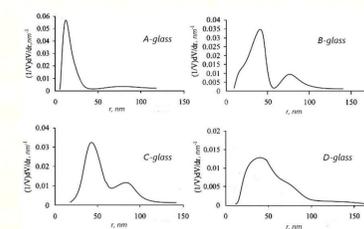


Fig. 3. Pore size distribution for different types of porous silicate glass.

