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## STUDY OF Se-BASED MICROGEL CATALYST FOR HETEROPHASE BENZALDEHYDE OXIDATION

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**Benzaldehyde was oxidized with hydrogen peroxide in the heterophase system with different ratios of benzene and water using selenium-based catalysts. For the reaction, which was carried out in the ratio of benzene:water = 4:1, Se-microgel proved to be a highly active colloidal catalyst and allowed to achieve 94.1 % yield of benzoic acid at 60 °C. The synthesized Se-modified microgel demonstrates exceptional catalytic activity in oxidation reactions at the interface in various heterophase systems at different temperatures.**

**Key words:** catalysis; benzaldehyde; oxidation; heterophase systems; microgel catalysts.

### Introduction

Recently, there has been great interest in the development of cost-effective materials and processes that eliminate the use of harmful substances and the generation of toxic waste. Heterogeneous catalysis can play a key role in the development of environmentally friendly chemical reaction processes in the petroleum and chemical industries [1, 2]. Today, heterogeneous catalysts are used more frequently due to numerous advantages over homogeneous catalysts, including ease of separation, regeneration, and recycling. On the other hand, homogeneous catalysts have good accessibility to catalytically active centers and high product selectivity [3]. Another approach to facilitate the separation and purification of products is to carry out the reaction in a two-phase medium ("water-oil"), when the initial reactants are in one phase and the products are in the other [5]. The growing interest in such a two-phase system is due to the use of environmentally friendly conditions – reactions are carried out in an aqueous medium [2]. Since the organic substances used as starting materials are insoluble in water, surfactants are often used to accelerate this type of reaction. However, the disadvantage of this approach is the problem of separating the surfactant from the product and catalyst with the possibility of its reuse for the next reaction cycle.

Therefore, an important scientific and technical task is to develop a new type of catalyst that can combine the advantages of hetero- and homogeneous catalysts and have the following characteristics: large surface area, narrow pore size distribution, the possibility of easy introduction of functional groups, accessibility for diffusion of reagents during the reaction, non-toxicity, resistance to corrosion and air, and suitability for reuse without loss of activity [4]. To date, several attempts have been made to functionalize carbon nanotubes with catalytically active sites, such as Pd and Au nanoparticles. However, despite the fact that these catalysts show promising results, their catalytic characteristics are not satisfactory: conversion, selectivity and yield of reaction products are low [1, 5, 6]. In addition, the catalytic activity decreases significantly after the 1st cycle [2, 7, 8], which leads to significant catalyst losses during recycling, washing and drying [8].

Microgels are soft multifunctional cross-linked polymeric colloids swollen in water or other solvents [9]. Due to their colloidal nature, microgels can be used as colloidal building blocks that can self-assemble at various interfaces to form functional colloidal superstructures. Previously, we reported the synthesis and characterization of selenium-modified microgels with a 3D polymeric network structure of

PVCL (poly(N-vinylcaprolactam)) microgels with enzyme-like activity in the process of homogeneous oxidation of acrolein by hydrogen peroxide. As a result, we obtained acrylic acid and methyl acrylate in high yields and selectivity [9, 10]. In this paper, we describe the catalytic activity of Se-modified microgels in the oxidation of benzaldehyde to produce benzoic acid in a two-phase benzene/water system.

### Materials and research methods

As reagents, we used benzaldehyde (99.9 % p.d.a., Across; hydrogen peroxide (60 %) p.d.a., Across. As a solvent, benzene (99 %) p.d.a. The following catalysts were tested: diphenyl diselenide (DPDS), selenic acid ( $H_2SeO_3$ ), diselenide crosslinker (X-linker), and microgel catalyst modified with selenomethane (Se 2.0).

The reaction was carried out in a 25 mL batch reactor with constant stirring. The volume of the reaction mixture was 2 ml. The catalyst concentration,  $C = 0.0044$  mmol/ml. The reaction mixture was prepared with the addition of benzene as a solvent, benzaldehyde,  $C = 2$  mmol/mL, and an oxidizing agent, water solution of hydrogen peroxide,  $C = 2.6$  mmol/mL.

The research results were analyzed by gas chromatography: Agilent 6890 chromatograph with Restek Stabilwax-DA column.

### Results and discussion

In our previous work, we reported the synthesis of a microgel based on Poly-N-vinyl caprolactam (PVCL) with a conventional crosslinker N,N'-Methylenebis(acrylamide) (BIS), 1.5 % mol, and a diselenide crosslinker, 2 % mol, containing diselenide functional groups [9, 10]. When hydrogen peroxide is added, the diselenide crosslinker is cleaved and a catalytically active perselenic acid functional group ( $-SeOOH$ ) is formed. This composition of the modified Se catalyst (BIS 1.5 % Se 2.0 %) showed the best results in the homogeneous oxidation process and was therefore chosen to study the oxidation process under heterogeneous conditions (Fig. 1).

The catalytic activity of the Se-modified microgel (Se 2.0) was evaluated in a model benzaldehyde oxidation reaction using hydrogen peroxide as an oxidant in a two-phase reaction (benzene/water). In this system, the reactant and product (benzaldehyde and benzoic acid) are in the organic phase, and the oxidant (hydrogen peroxide) is in the aqueous phase.

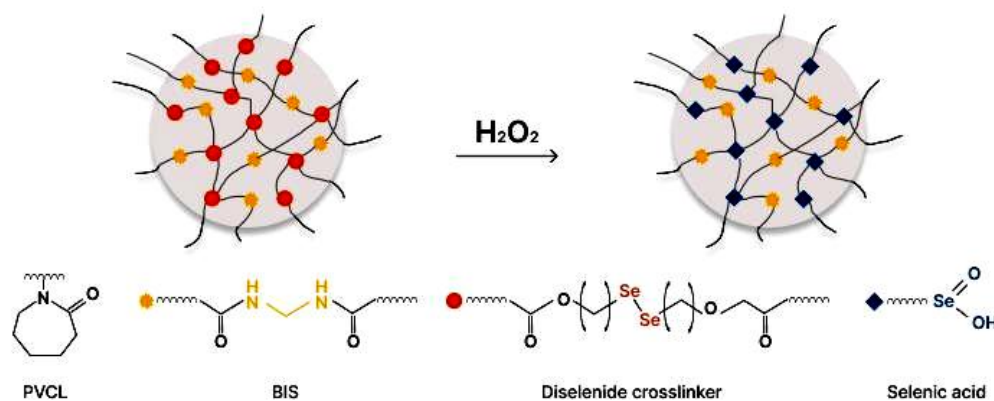


Fig. 1. Transformation of Se-based PVCL under the influence of hydrogen peroxide ( $H_2O_2$ )

Two different heterogeneous systems were tested in the course of the research: benzene:water volume ratio = 1:4 and benzene:water = 4:1. When the reaction was carried out in an environment with a large excess of water, the yield of benzoic acid was quite low, not higher than 30 % (Fig. 2). This result can be explained by the inhibition of the oxidation reaction by water. For the reaction carried out in the

ratio of benzene:water = 4:1, Se-microgel proved to be a highly active colloidal catalyst and allowed to achieve 94.1 % yield of benzoic acid at 60 °C (Fig. 2).

The influence of the nature of the catalyst on the yield of benzoic acid was investigated. During the studies at a temperature of 30 °C, a benzoic acid yield of 68.8 % was obtained, which is twice as high as for the Se crosslinker (X-linker) and  $H_2SeO_3$  (Fig. 3, a).

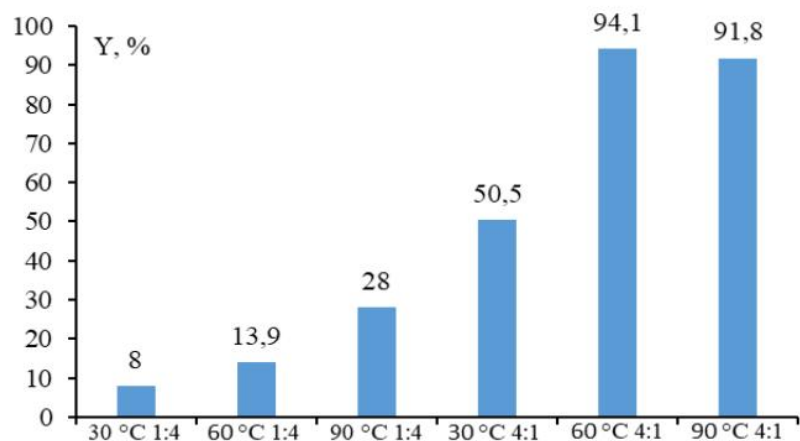


Fig. 2. Influence of the ratio of benzene to water and reaction temperature on the yield of benzoic acid (Y). The catalyst is B 1.5 Se 2.0

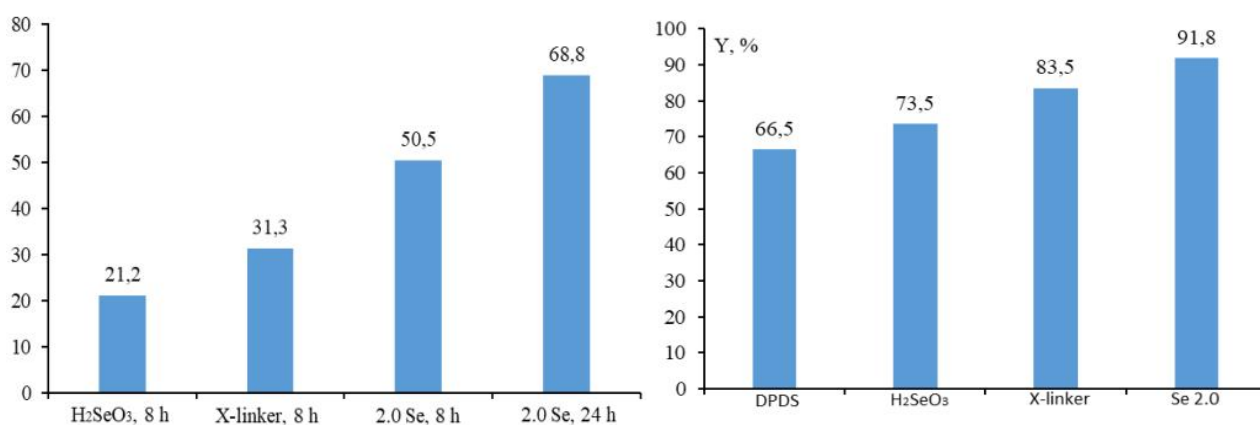


Fig. 3. Effect of the catalyst on the yield of benzoic acid (Y). Benzene:water ratio = 4:1, reaction temperature – 30 °C (a); Effect of the nature of the catalyst on the yield of benzoic acid (Y). Benzene:water ratio = 4:1, reaction temperature – 90 °C Reaction time – 8 hours (b)

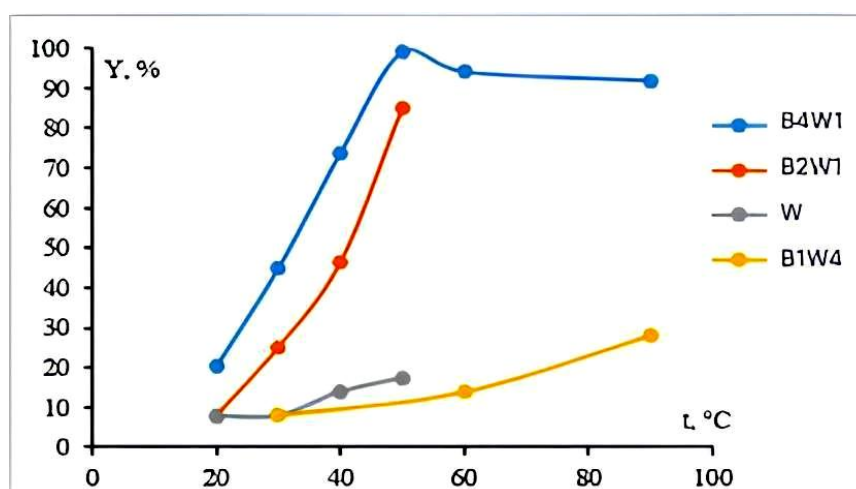


Fig. 4. Effect of Benzene / water ratio and reaction temperature on the yield of benzoic acid (Y). The catalyst is Se 2.0. Where B4W1, B2W1, W, B1W4 is benzene:water ratio

Low-molecular-weight catalysts such as diphenyl diselenide (DPDS) and selenic acid ( $\text{H}_2\text{SeO}_3$ ) show lower results compared to high-molecular-weight catalysts such as diselenide crosslinker (X-linker) and Se 2.0 microgel. During the study, at a benzene:water ratio of 4:1, reaction temperature of 90 °C, and reaction time of 8 h, the yield of benzoic acid using the Se 2.0 microgel catalyst was 91.8 %, which is the highest compared to other catalysts, indicating excellent surface-active properties of the developed catalyst (Fig. 3, b).

To evaluate the catalytic properties of Se 2.0 microgel at the interface, four heterophase systems were used: “water in oil” (benzene:water ratio = 4:1 and 2:1), “oil in water” (benzene:water ratio = 1:4) and water, since the reagent and the reaction product are insoluble in water (Fig. 4). When the reaction was carried out in a system without excess benzene (benzene:water ratio 1:4), the yield of benzoic acid was quite low. This phenomenon can be explained by the inhibitory effect of water on oxidation reactions, as mentioned earlier. On the other hand, preliminary studies of the colloidal properties of microgels in water-in-oil and oil-in-water systems showed that water droplets are formed in oil regardless of the ratio of oil and water phases. In the oil-in-water emulsion system, the reagent (benzaldehyde) is concentrated in the benzene phase, which is surrounded by the microgel, while the oxidant (hydrogen peroxide) is concentrated mainly in the aqueous part, and the reaction occurs at the oil/water interface in the microgel. In this case, a lower concentration of hydrogen peroxide is observed at the interface due to excess water and a higher concentration of benzaldehyde. A slightly higher yield in the water compared to benzene:water ratio 1:4 system is likely due to higher concentration of benzaldehyde in the organic phase. In the water-in-oil system, the situation is the opposite – a lower concentration of benzaldehyde due to excess benzene, and a higher concentration of hydrogen peroxide.

Based on the results obtained, it can be concluded that the optimal benzene:water ratio is 4:1. The highest yield of benzoic acid at this ratio may be due to the higher concentration of the oxidant.

### Conclusions

The synthesized Se-modified microgel is a highly efficient colloidal catalyst in heterophase

reactions. It demonstrates exceptional catalytic efficiency in the oxidation of aldehydes by the “green” oxidizing agent hydrogen peroxide. It shows high results in various heterophase systems over a wide temperature range.

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**ДОСЛІДЖЕННЯ МІКРОГЕЛЕВОГО КАТАЛІЗАТОРА  
НА ОСНОВІ Se В РЕАКЦІЇ ГЕТЕРОФАЗНОГО  
ОКИСНЕННЯ БЕНЗАЛЬДЕГІДУ**

Бензальдегід окиснювали пероксидом водню у гетерофазній системі з різним співвідношенням бензолу і води з використанням каталізаторів на основі селену. Для реакції, яку проводили у співвідношенні бензол:вода = 4:1, Se-мікротель виявився високоактивним колоїдним каталізатором і дав змогу досягти 94,1 % виходу бензойної кислоти за 60 °С. Синтезований мікротель, модифікований Se, демонструє виняткову каталітичну активність у реакціях окиснення на межі поділу фаз у різних гетерофазних системах, за різних температур.

**Ключові слова:** каталіз; бензальдегід; окиснення; гетерофазні системи; мікротелеві каталізатори.