Se-modified microgels as efficient colloidal catalysts for heterophase oxidation reactions

Roman Nebesnyi[1], Anastasia Pavliuk[1], Kok Hui Tan[2], Tetiana Kharandiuk[2], Volodymyr Ivasiv[1]

1. Lviv Polytechnic National University, S. Bandery st. 12, Lviv, Ukraine;

2. DWI - Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, Aachen, Germany

New highly efficient colloidal Se-modified microgel catalyst was synthesised. It shows exceptional catalytic performance in heterophase aldehyde oxidation reaction with green hydrogen peroxide oxidant at mild reaction temperature.

Keywords – microgel, oxidation, heterophase reaction, catalysis, acrolein, acrylic acid.

Introduction

Reactions in heterophase (water/oil) conditions attract more attention due to more environmentally friendly conditions - reactions are performed in aqueous media, easier product separation and purification. But organic reactants usually are not soluble in water. Surfactants are often used to facilitate reactions but it can be problematic to separate surfactant from product and catalyst is still needed for the reaction. Good solution for these issues would be heterogeneous catalyst with surfactant ability. Microgels are soft multifunctional crosslinked polymer colloids with tuneable chemical composition, functionality and particle architecture, that can be swollen in water or other solvents. Previously we reported synthesis and characterization of Selenium modified microgels and their high catalytic activity in homogeneous oxidation process of acrolein with hydrogen peroxide as green oxidant [1]. Here we report the study of Se-modified microgel in heterophase oxidation reaction of benzaldehyde to benzoic acid as model reaction.

Methods

Poly(N-vinylcaprolactam) (PVCL) microgel modified with diselenide functional groups (diselenide crosslinker, 2% mol.) was synthesized by precipitation polymerization in aqueous/DMSO media at 70°C along with conventional crosslinker N,N'-Methylenebis(acrylamide) (1.5 %) according to the reported procedure [1]. Diselenide bonds inside the microgel were cleaved through oxidation by H_2O_2 and converted to catalytically active seleninic peracid whilst maintaining the microgel microstructure intact. Catalytic performance of Se-modified microgel (Se-μG) was evaluated in benzaldehyde oxidation reaction with H_2O_2 (60%wt.) as oxidant (benzaldehyde: H_2O_2 ratio - 1:1.3) judged by the yield of benzoic acid.

Results and discussion

Two heterophase systems were used: “water in oil” (toluene:water ratio - 4:1) and “oil in water” (toluene:water ratio - 1:4). Catalytic performance of Se-modified microgels was compared to H_2SeO_3 and diphenyl diselenide (DPDS) - highly active catalysts in oxidation reaction [2] and diselenide crosslinker (X-linker) that don’t have surfactant properties (Fig. 1).
When reaction was performed in medium with large excess of water (“oil in water”), benzoic acid yield was quite low (Fig. 1a). This phenomenon can be explained by inhibitory effect of water on the oxidation reactions as has been reported before [2]. On the other hand, previous studies of microgel colloidal properties in “water in oil” and “oil in water” systems shown that there are droplets of water formed in oil regardless the proportion of oil and water phases [3]. In the emulsion system “oil in water” reactant (benzaldehyde) is concentrated in toluene phase, which are surrounded by microgel while oxidant (hydrogen peroxide) is concentrated mainly in water part and the reaction occurs at the “oil/water” interface in the microgel. In this case, at the

interface we have proportion of reactant:oxidant=4:1, but in the system “water in oil” we have opposite proportion - reactant:oxidant=1:4. Such excess of oxidant might promote oxidation and therefore cause much higher yield of the product.

Furthermore, if we compare results of H_2SeO_3 that has no surfactant activity with Se-modified microgel in both “oil in water” and “water in oil” we can see that both catalyst shown higher catalytic performance in “water in toluene” system (Fig. 1a). Se-μG has higher catalytic activity in both systems due to reaction occurring inside the micrgel particles where reactants from both liquid phases can freely interact with catalytic Se groups, so the microgels can be considered as catalytic microreactors.

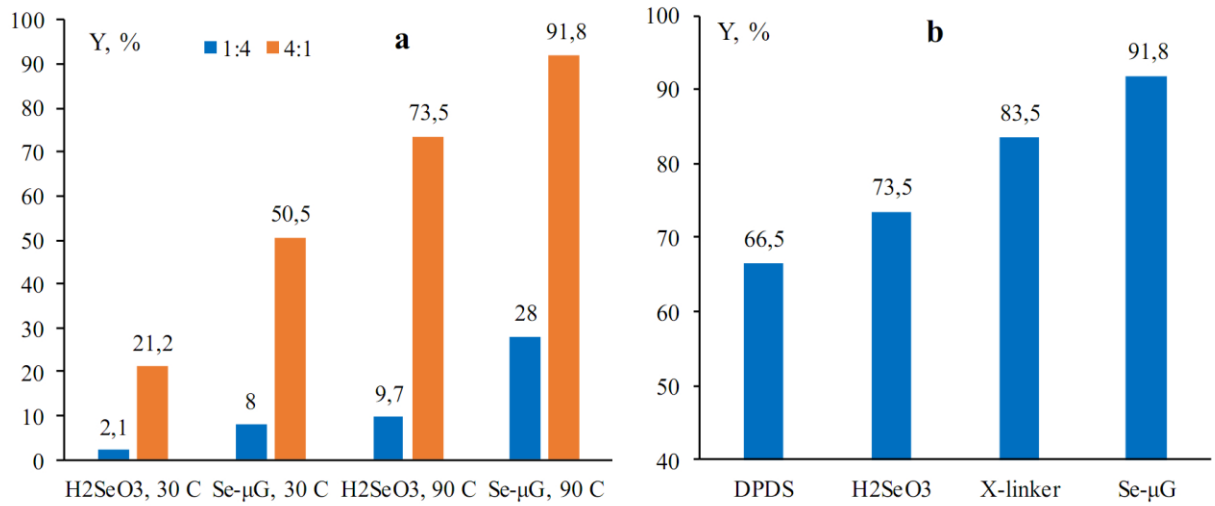

Fig.1. (a) Effect of toluene:water ratio, catalyst and reaction temperature on the yield of benzoic acid (Y), reaction time - 8 h. (b) Effect of catalyst on the yield of benzoic acid (Y), toluene:water ratio=4:1, reaction temperature - 90 °C, reaction time - 8 h.

Catalytic performance of Se-μG was compared with other Se-containing catalysts (Fig. 1b). Se-modified microgel shown the highest catalytic activity among studied catalysts and allows to achieve 91.8 % yield of benzoic acid already after 8 h of the reaction.

Conclusions

Newly synthesised Se-modified microgel is highly efficient colloidal catalyst at heterophase reaction conditions. It shows exceptional catalytic performance in aldehyde oxidation reaction with green oxidant hydrogen peroxide. Even at mild reaction temperature (30 °C) Se-μG proved to be highly active catalyst.

References

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