Se-driven microgel catalysts for interfacial oxidation reactions

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New efficient colloidal Se-modified microgel catalysts of various structures were synthesized and characterized. 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, benzaldehyde, benzoic acid, dithiothreitol.

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 and dithiothreitol oxidation as model reactions.

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

Three heterophase systems were used: "water-in-oil" (toluene:water ratio 4:1), "oil-in-water" (toluene:water ratio 1:4), and toluene:water ratio 1:1. We compared the catalytic properties of Se-modified microgels in different heterophase systems (Fig. 1a). When the reaction was carried out in a system without toluene excess (toluene:water ratio 1:4 and toluene:water ratio 1:1), the yield of benzoic acid was rather low (Fig. 1a). This phenomenon can be explained by the inhibitory effect of water on oxidation reactions. On the other hand, previous studies of the colloidal properties of microgels in the "water-in-oil" and "oil-in-water" systems showed that water droplets were formed in oil regardless of the ratio of the oil and water phases [3]. In the oil-in-water emulsion system, the reactant (benzaldehyde) is concentrated in the toluene phase, which is surrounded by the microgel, while the oxidant (hydrogen peroxide) is concentrated mainly in the water part, and the reaction occurs at the oil/water interface in the microgel. In this case, at the interface there is lower concentration of hydrogen peroxide due to excess of water, and higher concentration of benzaldehyde. In the system "water in oil" situation is opposite – lower concentration of benzaldehyde due to excess of toluene, and higher concentration of hydrogen peroxide. Based on the obtained results, we can conclude that the optimal toluene:water ratio is 4:1 by both yield and selectivity of benzoic acid. Highest benzoic acid yield at this ratio may be caused by higher oxidizer concentration while lower benzaldehyde concentration may attribute to high benzoic acid selectivity.

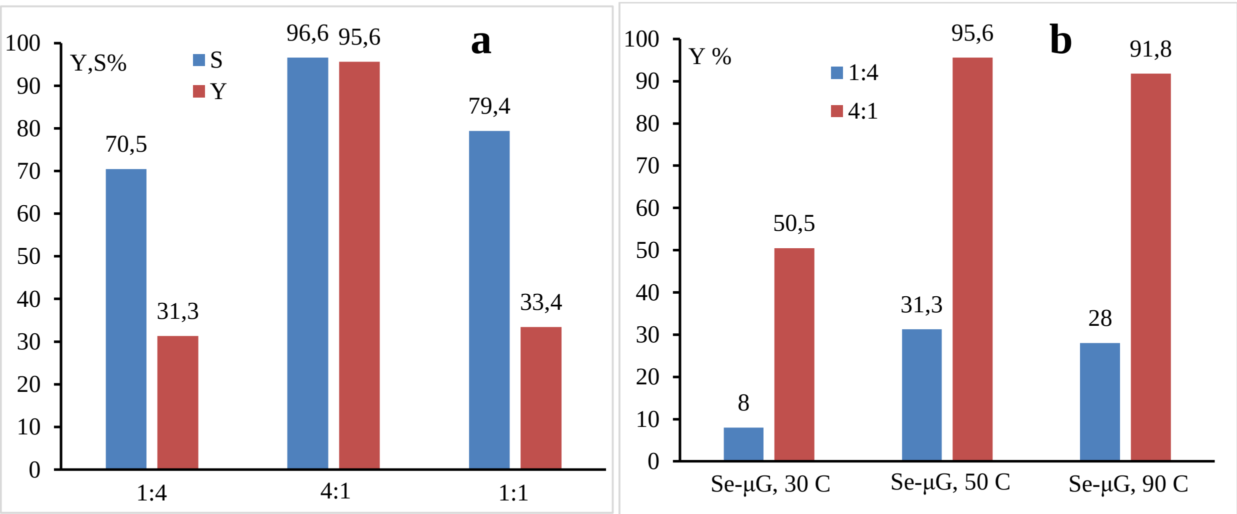

Fig.1. (a) Effect of toluene:water ratio on the selectivity (S) and yield (Y) of benzoic acid, reaction temperature - 50 °C, reaction time - 8 h. (b) Effect of temperature on the yield of benzoic acid (Y), toluene:water ratio = 4:1 and 1:4, reaction temperature – 30, 50, 90 °C, reaction time - 8 h.

Also the catalytic properties of Se-modified microgels in heterophase systems "water in oil" (toluene:water ratio 4:1) and "oil in water" (toluene:water ratio 1:4) were compared at different reaction temperatures (Fig. 1b). Based on the obtained results, the optimum reaction temperature is 50 °C, since with increasing the reaction temperature to 90 °C the yield of benzoic acid slightly decreases due to formation of by-products.

Conclusions

The newly synthesized Se-modified microgel is a highly efficient colloidal catalyst under heterophase reaction conditions. It demonstrates exceptional catalytic efficiency in the reaction of oxidation of aldehydes by the green oxidant hydrogen peroxide. It shows high results in different heterophase systems and in the reaction at different temperatures.

References

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