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Promoting the Activity of Bifunctional Catalysts for Autoxidation of 1-Octanethiol

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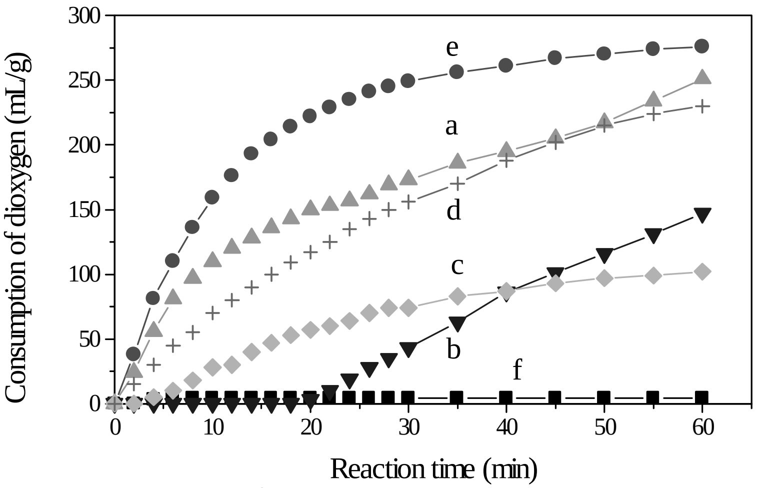
Abstract: Methanol and detergent are chosen to be additives for the catalysts derived from active carbon supported MgO and cobalt phthalocyanine (CoPc) or CoPc/NaY zeolite, and dramatically improved the activity and stability of catalyst in autoxidation of 1-octanethiol.

Keywords: Additive, 1-octanethiol autoxidation, CoPc/SiO_2, CoPc/NaY zeolite.

Mercaptans in petroleum products wreck the quality of finished products, so it is necessary to remove them in petroleum refining industry. Merox fixed-bed process is widely used in which mercaptans are converted by contacting feedstock with a metal phthalocyanine catalyst in the presence of air and an alkaline agent. However, use of caustic brings a spent caustic disposal problem so that novel caustic-free catalysts are highly desired to meet environment requirements[1-3]. It is not just simply a substitution of base because the new catalysts based on solid bases show a relative low activity and stability[4-5]. Unfortunately, little is known for the reason provoking these differences. In general the catalyst system also contains onium species and polar compound as additive, but most of the investigations focus on modification of metal chelate or alkaline agent and little attention is paid on the function of additive. In this paper we try to report a novel method of using additive to improve the activity and stability of bifunctional catalyst for autoxidation of 1-octanethiol.

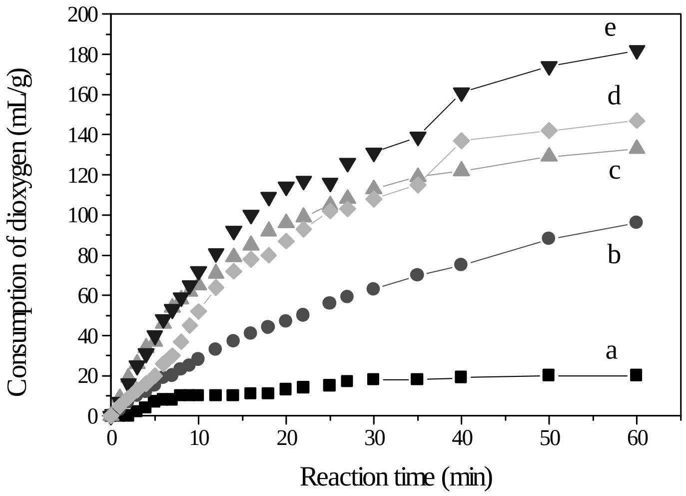
Carrier A is the active carbon supported MgO (10 wt.-%)[6] and B is the silica with a surface area of 350 m^2/g, both catalyst A and B contain CoPc species of 1 wt.-% by soaking carrier in methanol solution of CoPc. CoPc species is added in gel phase during synthesis of zeolite to prepare the catalyst C[7] and the resulting material CoPc/NaY has an XRD patterns the same as that of zeolite NaY except the blue color. Autoxidation of 1-octanethiol is performed in a sealed flask where 100 mg of catalyst has been soaked in octane (10 mL) beforehand with stirring while the flask is purged with oxygen. When the pressure of oxygen is kept constant at 313 K, 1- octanethiol of 1 mL is injected to start the reaction, and the consumption of oxygen represents activity of catalyst. To examine the influence of additive, methanol (AR grade) or a common powder detergent with trademark of Jia-jia is added into the flask prior to reaction.

Figure 1 Oxidation of 1-octanethiol at 313 K over catalyst A



(a) as-prepared, (b) dried in air for 20 days and adsorbed moisture, (c) mixed with K_2CO_3 of 5 wt.-%, (d) sample c soaked in methanol of 20 mL/g, (e) sample d was added detergent of 2 wt.-%, and over (f) the methanol solution of detergent.

Figure 2 Oxidation of 1-octanethiol at 313 K on catalyst B

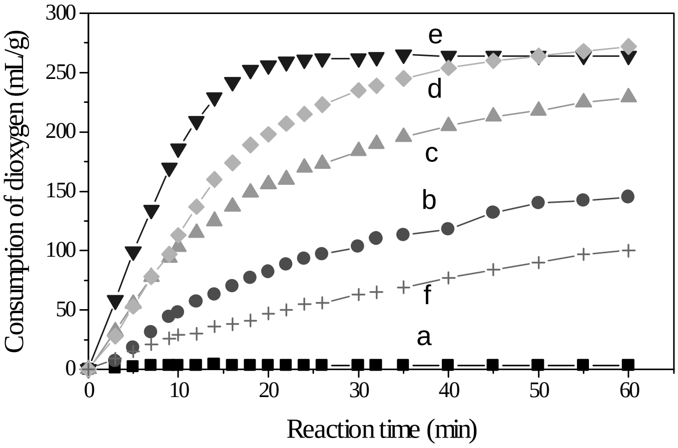


(a) before and (b-e) after soaked with methanol of 20 mL/g and added detergent of (c) 2 wt.-%; (d) 5 wt.-%; (e) 17 wt.-%.

Figure 1 shows the oxidation of 1-octanethiol on catalyst A at 313 K. The fresh sample exhibited a relative high activity with an oxygen consumption of 251 mL/g at 1 h, meaning about 39.5 mmol 1-octanethiol to be converted. After drying in air for 18 days, its activity dramatically decreased and the oxygen consumption at 1 h was 142 mL/g. Adsorption of moisture could not recover the activity while mixing with K_2CO_3 partially improved the catalytic property of the sample, especially in the first 0.5 h. However, soaking with methanol obviously increased the activity, closely matching to that of fresh sample; in contrast soaking in ethanol or 2-propanol had no promotion but caused separation of catalyst and reactant. Based on these facts it is very likely that the role played by methanol in this system is not proton transfer; otherwise three additives should have the same improvement on catalyst because all of them were proton transfer[1]. Methanol situates in between water and ethanol but only it can enhance the activity of catalyst in 1-octanethiol oxidation. Due to its solubility in both water and benzene, methanol may improve the surface state of catalyst contacted with the oil reactant. In order to pursue this point further, a detergent is chosen as additive because it has surface-active agent with both hydrophilic and hydrophobic groups, and can also improve the surface state of catalyst. As expected, a rather high activity was thus provoked on the catalyst with an oxygen consumption of 276 mL/g at 1 h exceeding that on the fresh sample. In contrary the methanol solution of detergent was inactive in reaction, excluding the possibility that the basic component in detergent catalyzed 1-octanethiol oxidation.

Figure 2 proves the promotion of methanol or detergent on catalyst B. This sample showed a low activity due to the lack of basicity. Soaking with methanol increased the activity 4 times high while adding detergent with 2 or 5 wt.-% enhanced the activity up to an oxygen consumption of 133 or 147 mL/g, but addition of more detergent did not provoke further improvement. **Figure 3** demonstrates the improvement of methanol and detergent on the activity and stability of catalyst C in which CoPc has been well dispersed in zeolite[7]. The original activity of the sample was quite low, similar to those bifunctional catalysts reported in 1-octanethiol oxidation[4]. Soaking in methanol and adding detergent provoked a very high and stable activity on catalyst C, and it kept an oxygen consumption about 100 mL/g at 1 h in the 10th run, still several times higher than the original activity. The total oxygen consumption after the 12th run reached 2150 mL/g, indicating about 338.8 mmol/g of 1-octanethiol had been oxidized in the experiment.

Figure 3 Oxidation of 1-octanethiol at 313 K on CoPc/NaY



(a) before and (b-f) after soaking in methanol of 20 mL/g and adding detergent of 5 wt.-% and used for (b) 1st, (c) 2nd, (d) 4th, (e) 6th and (f) 10th run.

Adjusting surface state seems to be decisive to improve activity and stability of the catalyst for autoxidation of mercaptans, because establishing a suitable micro-environment where active sites exist and contact reactant is crucial for preparation of an efficient catalyst. The key step is to discover cheap additive and to explore the mechanism of improvement in future.

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