

Cobalt-iron magnetic composites as heterogeneous catalysts for the aerobic oxidation of thiols under alkali free conditions

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Introduction

Oxidative coupling of thiols (mercaptans) is a very important reaction in chemical and petroleum industries [1]. Disulfides find various direct industrial applications, e.g., in vulcanization of rubbers and elastomers. On the other hand, the oxidation of mercaptans into innocuous disulfides (the Merox process) is the most widely employed technique in the petroleum industry for the preparation of high quality fuels. Most methods reported for the synthesis of disulfides use stoichiometric oxidants, such as dichromates, permanganates, or metal peroxides [2,3]. Catalytic oxidation of thiols using molecular oxygen as a final oxidant is obviously a much more attractive alternative. The most studied catalysts for this reaction are cobalt phthalocyanine complexes, employed in both the petroleum industry and the commercial-scale syntheses of disulfides [1,4]. Besides the disadvantage of using relatively high price catalysts, these reactions require strongly alkaline conditions to be efficient.

The aim of the present work was to use an inexpensive iron oxide-rich soil for the preparation of cobalt containing magnetic materials and to study the behavior of these materials as heterogeneous catalysts in liquid-phase oxidation reactions. We have developed a simple and efficient process for the aerobic oxidation of thiols into disulfides under mild conditions in the absence of alkaline co-catalysts. In this process, cobalt-iron composites easily prepared from low cost cobalt and iron precursors are used as heterogeneous magnetically recoverable catalysts. The catalysts provide near-quantitative yields and undergo no metal leaching.

Experimental

The iron oxide-rich soil was impregnated with water containing sucrose, CoSO_4 and H_2SO_4 . The mixture was heated at 110 °C to evaporate the solvent. The solid was treated for at 800 °C in air. The cobalt content in the samples was determined using a Spectro Modula ICP-OES instrument. Surface areas were determined using a Autosorb 1 Quantachrome gas sorption analyzer. X-ray diffraction (XRD) was carried out using $\text{Co-K}\alpha$ radiation with a Rigaku

Geigerflex diffractometer. Mössbauer spectra were collected in a constant acceleration transmission mode with a 25 mCi $^{57}\text{Co}/\text{Rh}$ gamma-ray source. Reactions were carried out in a glass reactor open to air, which was equipped with a condenser and magnetic stirrer. Reactions were followed by gas chromatography (GC) (Shimadzu 17, Carbowax 20 M). The structures of the products were confirmed by GC/MS (Shimadzu QP2010-PLUS).

Results/Discussion

Cobalt-iron magnetic composites prepared by the thermal treatment of an iron oxide-rich soil in the presence of sucrose and CoSO_4 were found to be efficient heterogeneous catalysts for the liquid-phase aerobic oxidation of various thiols into corresponding disulfides. The materials were characterized by Mössbauer spectroscopy, XRD, N_2 adsorption-desorption, and elemental analysis. It has been shown that the isomorphic substitution of iron by cobalt occurs preferentially in the framework of the wüstite (FeO) phase and strongly affects the catalytic behavior of the material. The choice of a solvent is critically important for the efficiency of the reaction. Weakly basic solvents seem to participate in the activation of the substrate eliminating the need for alkaline co-catalysts, which are corrosive and waste generating. In dimethylformamide and dimethylacetamide as the solvents, disulfides were obtained in near-quantitative yields at very low catalyst loading (0.008 mol%).

A significant practical advantage of this environment-friendly process is the use of inexpensive magnetically recoverable materials as catalysts and oxygen as a final oxidant as well as mild alkali free conditions and a virtually 100% selectivity. The catalysts are stable toward leaching and can be recycled. After the reaction, the materials were easily recovered by the application of an external permanent magnet and re-used several times without any special treatment. The catalyst was magnetically fixed at the bottom of the reactor and the supernatant solution was taken off with a pipette. We believe that our work contributes to opening the perspectives for the use of abundant natural iron oxides as precursor materials to produce magnetic catalysts. Further studies are targeted towards the applications of the developed materials as catalysts for the aerobic oxidation of other substrates, such as biomass-based olefins.

References.

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