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Aerobic selective oxidation of benzyl alcohols to benzaldehyde catalyzed by bidentate Schiff base dioxomolybdenum(VI) complex immobilized on CPS microspheres

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ABSTRACT

The Schiff base reaction between aldehyde (AL) group-modified crosslinked polystyrene (CPS) microspheres, AL–CPS microspheres, and glycine (GL) was conducted, resulting in the microspheres ALGL–CPS, on which bidentate Schiff base ligand ALGL were chemically anchored. Subsequently, the coordination reaction between the ligand ALGL of ALGL–CPS microspheres and molybdenyl acetylacetonate ($MoO_2(acac)_2$) was carried out, obtaining a new immobilized dioxomolybdenum(VI) complex with bidentate Schiff base-type, CPS-[$MoO_2(ALGL)_2$] microspheres, namely a new heterogeneous dioxomolybdenum(VI) complex catalyst was prepared. The microspheres CPS-[$MoO_2(ALGL)_2$] were fully characterized by many means such as FTIR, UV/Vis absorption spectrum and AAS. They were used in the oxidation reaction of benzyl alcohol by molecular oxygen. The experimental results show that through the coordination reaction between ALGL–CPS microspheres and molybdenyl acetylacetonate ($MoO_2(acac)_2$), the immobilized Schiff base dioxomolybdenum(VI) complex can be smoothly prepared. In the oxidation reaction of benzyl alcohol with molecular oxygen as oxidant, the heterogeneous dioxomolybdenum(VI) complex catalyst, CPS-[$MoO_2(ALGL)_2$], has very high catalytic activity. Under the mild conditions such as at ordinary pressure of dioxygen and at a lower temperature of 90 °C, benzyl alcohol can be transformed to benzaldehyde with a conversion of 63% in 10 h. It is namely the yield of benzaldehyde because benzaldehyde is the single oxidation product. It is obvious that CPS-[$MoO_2(ALGL)_2$] has excellent catalytic selectivity, and it specially catalyzes the oxidation reaction of benzyl alcohol to benzaldehyde. It was found that the solvent polarity effects on the catalyst activity greatly. The weaker the polarity of the solvent, the higher the activity of the catalyst CPS-[$VO(SAAM)_2$] is and the higher the yield of benzaldehyde is.

1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds is one of the most important transformations in organic synthesis [1–3]. Traditionally, the oxidation of alcohols has been achieved with stoichiometric noxious inorganic oxidants. Recently, the selective catalytic oxidation of alcohols to carbonyl compounds over heterogeneous catalysts with molecular oxygen (aerobic oxidation) has attracted much attention from the viewpoint of establishing green and sustainable chemical processes [4–6].

Among the alcohol oxidation reactions, the oxidation of benzyl alcohol to benzaldehyde is an important organic reaction because of benzaldehyde applications. Benzaldehyde is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro-chemical industries [7–9]. In regard to the aerobic catalytic oxidation of benzyl alcohol using molecular oxygen over heterogeneous catalysts, many studies have been focused on using supported noble metal catalysts, e.g., Ru-, Pd- and Au-based catalysts due to their superior catalytic performance [10–12]. Nevertheless, the use of various less expensive transition metals, such as Mn-, Ni-, and Al-containing catalysts still need to be explored from an economic point of view [7,13,14] through their catalytic activity may be poorer than those of precious metals. In this work, we try to use the immobilized molybdenum(VI) complex as catalyst in the aerobic catalytic oxidation of benzyl alcohol to benzaldehyde.

The coordination chemistry of molybdenum(VI) has attracted considerable interest due to its biological importance as well as the importance of molybdenum(VI) complexes as catalysts in various oxidation reactions such as epoxidation and hydroxylation of olefins and oxidation of alcohols [15,16]. In the catalytic

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