AN EFFICIENT AEROBIC OXIDATION FOR p-XYLENE TO p-TOLUIC ACID CATALYZED BY COBALT (II) HYDROXAMATES WITH BENZO-15-CROWN-5

Hong-bo Li a, Meng-an Hao a, Chuan Qin a, Wen-bing Yang a, Xiao-ping Hu a and Sheng-ying Qin b*

a College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, P. R. China
b Department of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, P. R. China

Received April 16, 2007, accepted May 3, 2007

Abstract

Cobalt (II) hydroxamates with the benzo-15-crown-5 (B15C5) pendant have been synthesized and characterized. These complexes were successfully employed to the oxidation of p-xylene to p-toluic acid with air at 110°C under normal atmospheric pressure. The effects of the B15C5 pendant, the length of chain bonding of B15C5 in these complexes and the addition of alkali metal ions on the oxidation for p-xylene are also investigated by the comparison with the crown-free analogue.

Keywords: Cobalt (II) hydroxamates, benzo-15-crown-5, catalytic oxidation, p-xylene

INTRODUCTION

Substituted benzoic acids are very important materials in chemical and pharmaceutical industries [1, 2]. In recent years, although many studies on the oxidation of p-xylene to p-toluic acid (PTA) catalyzed by Co(OAc)2/NaBr/AcOH, Co(C18H35O2)2/NH4Br or Schiff base complexes have been reported. The yield (<60%) and selectivity (<25%) for p-toluic acid were

* Corresponding author. E-mail: li-honggg@163.com
very low under these conditions [3,4]. A recent work by us indicated that azacrown-functionalized Schiff base complexes showed much better catalytic oxidation activities due to the special configuration and function of the crown ether ring [5]. But hydroxamic acid complexes, a kind of tetradeutate complex, as catalyst for the oxidation of alkyl compounds were seldom reported [6,7]; furthermore studies on transition-metal hydroxamates with crown ethers have not been examined up to now. Crown ether rings endow special performance and characteristics owing to the hydrophobicity of the outer ethylene groups and the orderly arrangement of the inner oxygen atoms [8,9]. Of course, crown ether-containing hydroxamic acids can be conceived to bind cations in the crown ether cavity, in addition to coordination of a transition metal center via O₄ donor atoms. Co-complexation of a hard cation close to the transition-metal center is believed to play an important role in perturbing its oxygen-binding properties.

Herein, as part of a research program aimed at studying the effects of pendant crown ether rings and their alkali metal complexes on the catalytic oxidation performance of crown-functionalized transition-metal hydroxamates, a series of cobalt (II) hydroxamates with benzo-15-crown-5 (B15C5) and their uncrowned analogue (Scheme 1) was developed and employed to the catalytic oxidation of p-xylene to p-toluic acid with air. Compared with the crown-free analogue CoL₂, the effects of the B15C5 rings appended in the ligand, the length of the methylene chain (CH₂)n and the added alkali metal ions into the reactive system on the catalytic oxidation performance of CoLₙ² (n=1~3) (Scheme 1) was discussed in detail.

Scheme 1 Structures of cobalt (II) hydroxamates