



Catalytic oxidation of anilines into azoxybenzenes on mesoporous silicas containing cobalt oxide

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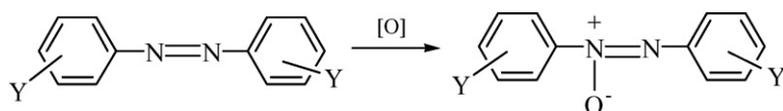
ABSTRACT

Synthesis of cobalt-bound copolymers and the use of this polymer as a template to prepare mesoporous silicas containing cobalt oxide are reported. This material catalyzed the oxidation of anilines into the corresponding azoxybenzene efficiently with the hydrogen peroxide as the oxidant. Furthermore, the catalyst can be recycled without losing the activity.

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1. Introduction

Azoxybenzene and its derivatives represent a new class of compounds displaying a broad range of potential application in materials because they have characteristic features emerging from the conjugated systems and polar functionality [1]. In addition, this type of compounds is the precursor for Wallach rearrangement, which offers a simple way to prepare hydroxyazobenzenes [1a,2]. Generally, the preparation of azoxybenzenes is via the direct oxidation of the corresponding azobenzene (Eq. (1)) and many oxidizing agents such as hydrogen peroxide [3], dimethyldioxirane [4], sodium perborate [5] and peracid [6] have been used for this process. In the use of H_2O_2 , Murray and coworkers found that the metal complex ($MeReO_3$) accelerated the oxidation to provide excellent yields of azoxybenzenes [3].



(1)

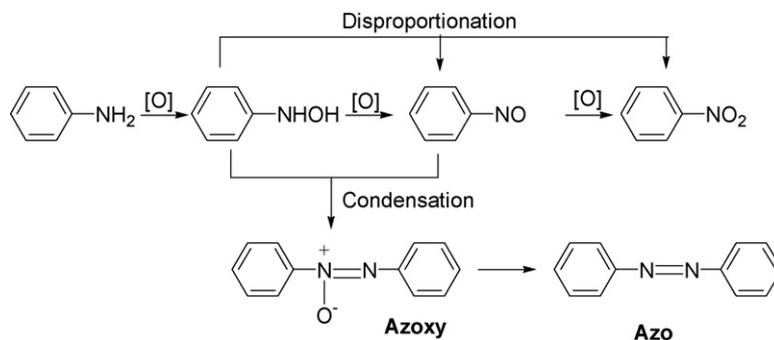
Azoxybenzene is known to be the intermediate from the oxidation of aniline or the reduction of nitroarene via the condensation of nitrosobenzene with *N*-phenylhydroxyamine. The oxidation steps of aniline leading to nitrobenzene are quite complex and a generally accepted mechanistic pathway is depicted in Scheme 1 [7]. Thus, manipulation of reaction conditions leading to the azoxy compound as a single product becomes a research interest for chemists. Till now, a few catalytic systems developed for this purpose have been reported [8–10]. Typically, these are perfluoroketone-silicate [8], polyoxometalate of a sandwich type structure [9] and titanium silicalite-1 (TS-1) [10]. Continuing our research on catalysis, we have developed a preparation of cobalt-containing mesoporous silica, which is active for the conversion of anilines into azoxybenzenes.

2. Results and discussion

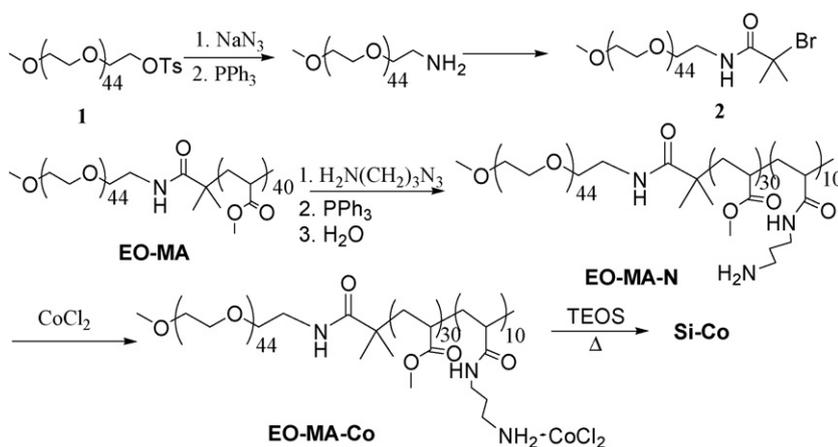
2.1. Preparation of catalyst

The cobalt-containing silicas (denoted as Si-Co) were synthesized through the condensation of tetraethoxysilane templated

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Scheme 1. Mechanistic pathway for oxidation of aniline.



Scheme 2. Preparation of the metal-containing diblock copolymer.

by the amphiphilic diblock (EO-MA-Co) copolymer under acidic conditions [11]. Starting with the tosylate of the methyl-capped polyethylene oxide $\text{Me}(\text{OCH}_2\text{CH}_2)_{45}\text{OTs}$ (**1**), the tosylate function was transformed into an amine function, which subsequently reacted with 2-bromoisoobutyric chloride to provide the macro-initiator poly(ethylene oxide)-2-bromoisoobutyrate (**2**) (Scheme 2). The formation of the amide linkage is required for keeping the copolymer intact during the further transformation of the diblock copolymers. A simple ester linkage formed from $\text{Me}(\text{OCH}_2\text{CH}_2)_{45}\text{OH}$ and 2-bromoisoobutyric chloride would undergo hydrolysis during the reactions. Compound **2** was subjected to connection with the poly(methyl acrylate) chain by the atom transfer radical polymerization method [12]. In a typical run, the reaction of macro-initiator (3.3 mmol) and methyl acrylate (MA) (55 mmol) at 30°C for 10 min resulted in the formation of the desired EO-MA of $M_N = 4500$ ($\text{PDI} = 1.14$). Based on the GPC and ^1H NMR integration, the polymerization degree of MA is in an average of 40 units. Treatment of the diblock copolymer with 3-aminopropyl azide provided the copolymer with the amido-linked side chain. The composition of the resulting modified copolymer (EO-MA-N), determined by ^1H NMR integration, included a 0.25-mole fraction of the azido group. Under anhydrous conditions, the copolymer reacted with triphenylphosphine to generate the iminophosphorane functionality [11,13], which was subsequently hydrolyzed to generate the amine function. Addition of CoCl_2 to an aqueous solution of the copolymer readily caused the color change from purple to blue, indicating the formation of its metal complex (EO-MA-Co).

By using the metal-bound diblock copolymer EO-MA-Co as the template, preparation of the desired materials under acidic conditions was achieved. Upon calcination at 560°C , the porous

silica Si-Co was obtained. X-ray diffraction patterns of the sample show that the mesophase of the resulting porous silica is disordered. However, nitrogen absorption–desorption isotherms (Fig. 1) showed that the pore dimension of Si-Co is 13.3 nm with surface area of $499\text{ m}^2/\text{g}$, typical of mesoporous materials and similar to those of related materials [11]. The content of cobalt species inside of channels was estimated to be 16.5 mg/g of silica via the analysis of ICP-mass determination. XPS analysis was carried out in order to determine the valence state of the cobalt species on silicas. The O 1s XPS peak at 531.8 eV was attributed mainly to the silicates. A detailed scan of the Co $2p_{3/2}$ area showed a peak at 783.3 eV, which is assigned to the binding-energy component of the cobalt oxide

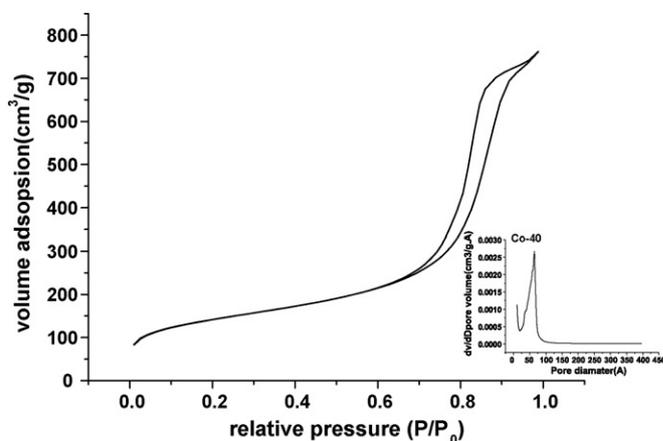


Fig. 1. Nitrogen absorption–desorption of Si-Co.

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