

Manganese oxide octahedral molecular sieve catalysts for synthesis of 2-aminodiphenylamine

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Abstract

Cryptomelane-type manganese oxides octahedral molecular sieve (K-OMS-2) were used for the acid-catalyzed condensation of phenylhydroxylamine with aniline to produce 2-aminodiphenylamine. The H⁺-exchanged K-OMS-2 was found to be an efficient catalyst for this reaction. The reaction showed high selectivity (~96%) for the *ortho* isomer of aminodiphenylamine compared with the *para* product. The effect of the amount of H⁺ exchange and temperature was investigated.

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1. Introduction

2-Aminodiphenylamine (ADPA) and its derivatives are compounds of great interest because of their numerous uses, including as precursors for the synthesis of biologically active compounds, as lubricant antioxidants, as fluorescent material, in dye formulations, and in polymer synthesis [1–4]. 2-ADPA also has great therapeutic importance [5]. In general, 2-ADPA is synthesized by reduction of the corresponding nitro compound; it has also been synthesized by the rhodium-catalyzed rearrangement of 1,2-diphenylhydrazine [6]. Synthesis of 2-ADPA (*ortho* isomer) has been reported in the literature mostly as a byproduct, with 4-ADPA (*para* isomer) as the major product [7,8].

Earlier researchers have reported that 4-ADPA can be produced by condensation of phenylhydroxylamine (PHA) and aniline in the presence of concentrated HCl or solid acids like H-ZSM-5, H-Y Zeolite, Nafion, Filtrol (acid clay), Dowex resin, and others [7,8]. This reaction yields predominantly the *para* isomer of aminodiphenylamine.

Octahedral molecular sieve (OMS) of manganese oxides have been typically used as oxidation catalysts [9–11]. In the present study, OMS was used as a catalyst for an acid-catalyzed condensation reaction of aniline with phenylhydroxylamine (PHA) to produce 2-ADPA. The catalyst used in the reaction is a cryptomelane-type manganese oxide OMS (K-OMS-2), with the composition $\text{KMn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$. K-OMS-2 is a mixed valent manganese oxide with Mn⁴⁺, Mn³⁺, and some Mn²⁺ sites. K-OMS-2 consists of MnO₆ octahedral units, which are edge- and corner-shared to form 4.6 × 4.6 Å tunnels as a result of 2 × 2 arrangements of octahedra. K⁺ ions are present in the tunnels with small amounts of water (Fig. 1). The K⁺ ions in the tunnel can be exchanged with H⁺ through ion-exchange methods.

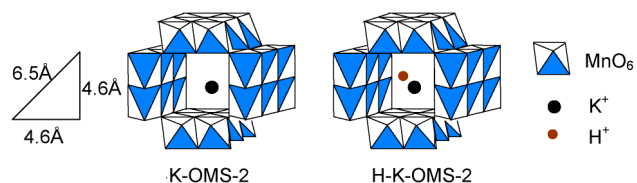


Fig. 1. Structure of OMS-2 catalysts.

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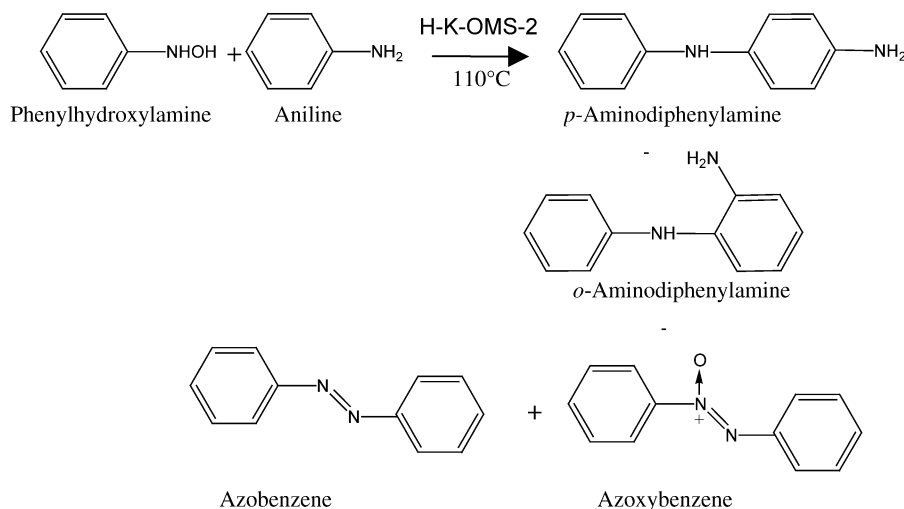


Fig. 2. Acid catalyzed condensation reaction of phenylhydroxylamine with aniline.

Herein we report the synthesis of 2-ADPA by a direct method in which it is obtained in high selectivity (~96%) compared with 4-ADPA. The process involves condensation of PHA with aniline over manganese oxide OMS (OMS-2), which was converted to the H⁺ form (H-K-OMS-2) by successive ion exchanges with different HNO₃ concentrations. PHA was contacted with aniline in a stirred semibatch reactor in the presence of H-K-OMS-2 in an inert atmosphere at 110 °C. The other products of this reaction, azoxybenzene and azobenzene, can be recycled to aniline by hydrogenation. The work reported herein focuses only on 2-ADPA and 4-ADPA (Fig. 2).

2. Experimental

2.1. Reagents

Aniline was supplied by Aldrich and was used without further purification. PHA was synthesized by chemical reduction of nitrobenzene with ammonium chloride and zinc dust according to the general method reported in the literature [12,13].

2.2. Catalyst synthesis

K-OMS-2 was prepared by refluxing a mixture of potassium permanganate and manganese sulfate in acidic medium as described previously [14]. K⁺ ions were then exchanged with H⁺ ions through ion exchange of K-OMS-2 with HNO₃ to obtain H-K-OMS-2. Then 50 mL of 1 M HNO₃ was added to 2.0 g of K-OMS-2, and the slurry was stirred vigorously at 80 °C for 6 h. The product was filtered and washed several times with double-distilled water (DDW). This procedure was repeated for successive ion exchanges to obtain greater H⁺ exchange in K-OMS-2. The product was dried at 120 °C for 12 h, then calcined at 280 °C for 6 h. The final material was named H-K-OMS-2, with a number in brackets indicating the number of times that it was exchanged with 1 M HNO₃. H⁺ exchange was also done with concentrated HNO₃ to obtain a higher exchange of K⁺ using the same procedure.

2.3. X-Ray powder diffraction studies

The structure of all the materials was studied by X-ray diffraction (XRD) experiments. A Scintag 2000 PDS instrument with Cu-K_α radiation with a beam voltage of 45 kV and a beam current of 40 mA was used to collect the X-ray data.

2.4. Chemical composition measurement

The chemical compositions of the synthesized catalysts were determined by energy-dispersive X-ray analysis (EDAX) on a Philips PV 9800 EDAX spectrometer using a SuperQuant program. This analysis provides a measure of the amount of H⁺ in the tunnel of K-OMS-2 that was exchanged with K⁺ cations.

2.5. Average oxidation state

The average oxidation state (AOS) of manganese in OMS-2 catalysts was determined by potentiometric titrations as described previously [15].

2.6. Reaction procedure

The reaction was carried out in a 25-mL three-necked round-bottomed flask fitted with a reflux condenser. Aniline (5 mL) and catalyst (0.20 g) were added to the flask and purged with N₂ gas, and the flask was heated to the required reaction temperature (110–160 °C). Then 0.10 g (0.92 mmol) PHA in 5 mL of aniline was added to the flask using a syringe pump (model 341A, Sage Instruments) over a period of 35 min under stirring conditions. Reaction was stopped 5 min after completion of the addition. The reaction mixture was filtered, and products were analyzed by a Beckman System Gold HPLC equipped with a Zorbax column (8.0 cm × 4.5 mm) and a variable wavelength detector using a wavelength of 290 nm. The eluent was water with 0.05 M ammonium acetate and acetic acid (pH 5.0 ± 0.3) and acetonitrile.

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