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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.

Keywords: OMS-2; Aminodiphenylamine; Phenylhydroxylamine

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 $KMn_8O_{16}\cdot nH_2O$. K-OMS-2 is a mixed valent manganese oxide with Mn^{4+}, Mn^{3+}, and some Mn^{2+} sites. K-OMS-2 consists of MnO_6 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.

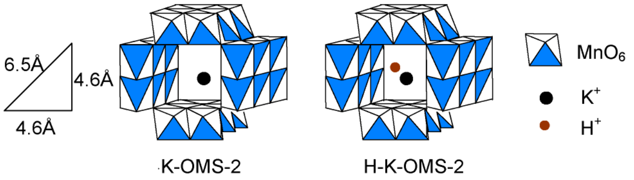

Fig. 1. Structure of OMS-2 catalysts.

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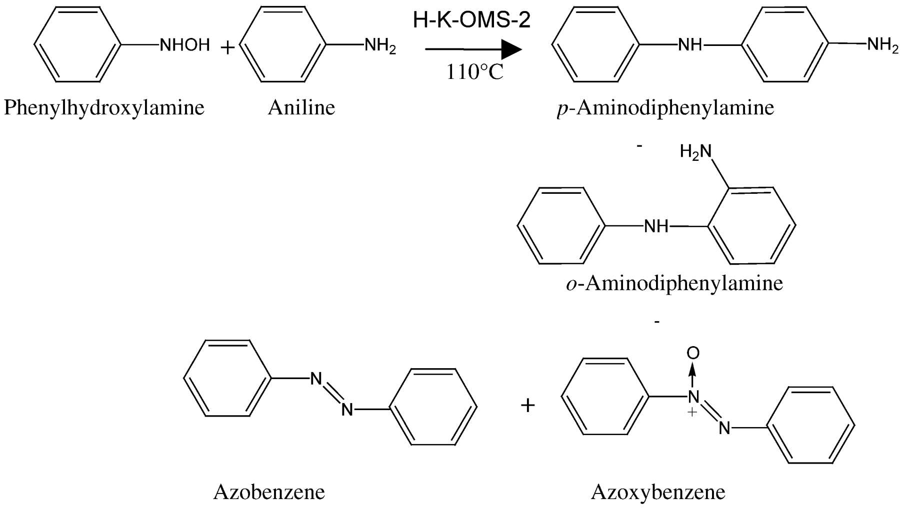

Fig. 2. Acid catalyzed condensation reaction of phenylhydroxylamine with aniline.

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 HNO_3 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 HNO_3 to obtain H-K-OMS-2. Then 50 mL of 1 M HNO_3 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 HNO_3. H^+ exchange was also done with concentrated HNO_3 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 N_2 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.

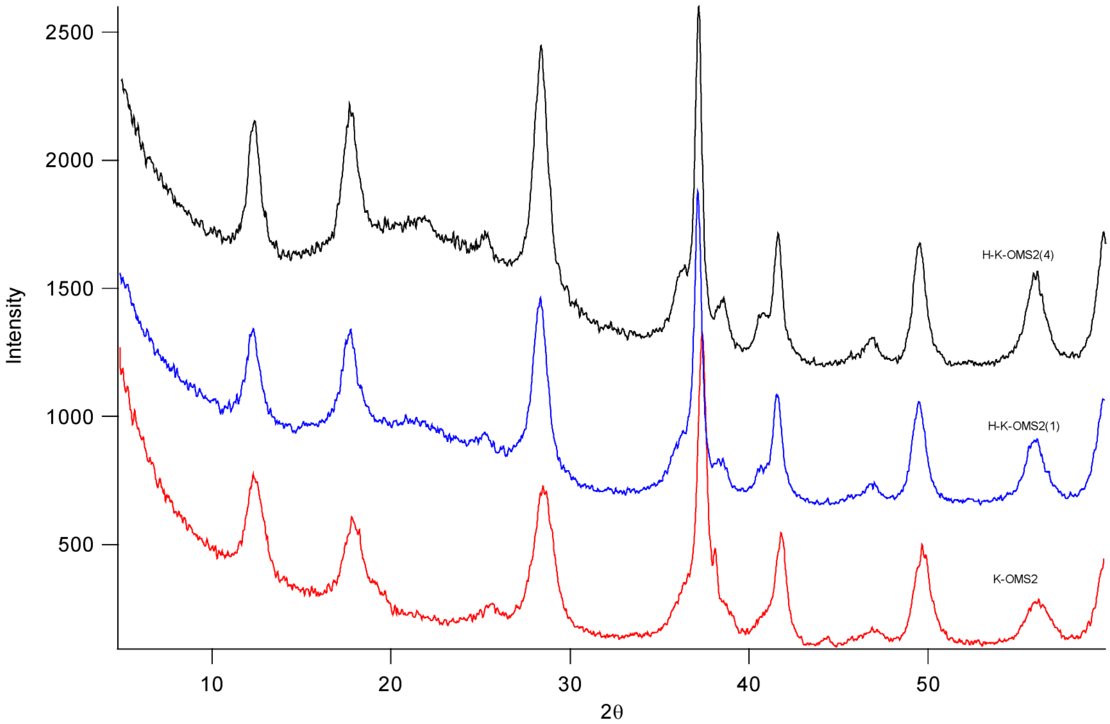

Fig. 3. X-Ray diffraction pattern of K-OMS-2 and H-K-OMS-2.

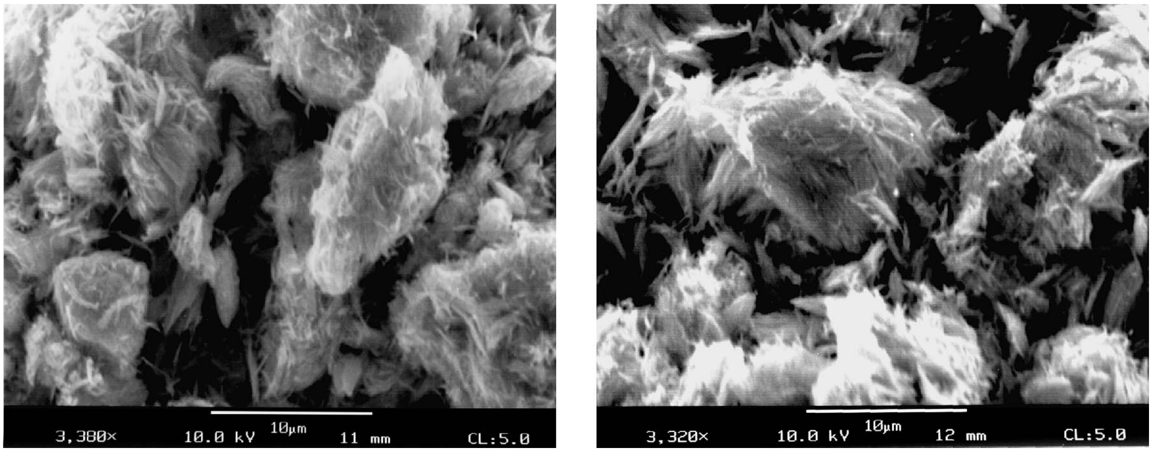

Fig. 4. SEM micrograph of K-OMS-2 and H-K-OMS-2.

3. Results

3.1. *X-Ray diffraction patterns*

Fig. 3 shows the XRD patterns of as-synthesized K-OMS-2 and after successive ion exchanges with H^+. These XRD patterns show that the catalyst retains its structure after successive ion exchanges with H^+.

3.2. *Chemical composition*

Scanning electron microscopy revealed a fibrous needle-like morphology for K-OMS-2 and a similar morphology for H-K-OMS-2 (Fig. 4). The tunnel cation substitution has no effect on the morphology. The amounts of K^+ cation in OMS-2 and in different H-K-OMS-2 materials were obtained from the EDAX analysis data. The percentage of K^+ exchanged with H^+ was calculated as shown in Table 1. After four successive exchanges with 1 M HNO_3, 40% of the K^+ was exchanged with H^+. When K-OMS-2 was exchanged with concentrated HNO_3, 50% of the K^+ was exchanged with H^+ after only two successive exchanges.

3.3. *Average oxidation state*

The AOS method can be used to determine the electronic environment around Mn centers. The average oxidation state of Mn in the as-synthesized K-OMS-2 was 3.81. The AOS of Mn decreases with an increasing extent of K^+ exchange by H^+, as shown in Table 3.

Table 1
Extent of H^+ in the synthesized catalysts and AOS of Mn

Catalyst	$\%K^+$ exchanged with H^+[a]	AOS
K-OMS-2	0	3.81
H-K-OMS-2(1)[b]	20	3.76
H-K-OMS-2(2)	28	3.69
H-K-OMS-2(4)	40	3.60
H-K-OMS-2(2C)[c]	50	3.54

[a] $\%K^+$ exchanged with H^+ was calculated based on the decrease in the wt% of potassium in EDAX data assuming that the amount of Mn does not change after the ion-exchange.

[b] The number in parentheses indicate the number of times K-OMS-2 was ion-exchanged with 1 M HNO_3.

[c] This catalyst was exchanged twice with concentrated HNO_3.

Table 2
Effect of various H-K-OMS-2 catalysts on selectivity

Catalyst	Temperature (°C)	%*Ortho* selectivity[a]
K-OMS-2	120	No reaction
H-K-OMS-2(1)	120	50.0
H-K-OMS-2(2)	120	83.3
H-K-OMS-2(4)	120	91.1
H-K-OMS-2(4)	110	94.2
H-K-OMS-2(2C)	110	95.9

[a] As determined by area % in HPLC analysis.

Table 3
Effect of temperature on selectivity

Catalyst	Temperature (°C)	%*Ortho* selectivity[a]
H-K-OMS-2(4)	110	94.2
H-K-OMS-2(4)	120	91.1
H-K-OMS-2(4)	130	86.8
H-K-OMS-2(4)	140	83.6
H-K-OMS-2(4)	150	73.7
H-K-OMS-2(4)	160	67.7

[a] As determined by area % in HPLC analysis.

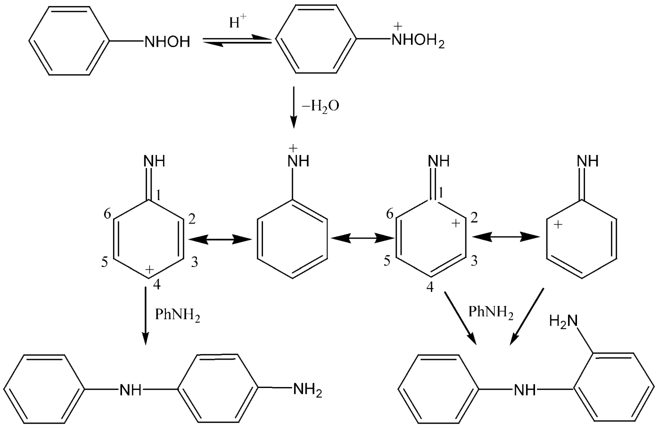

Fig. 5. Mechanism of acid catalyzed condensation of phenylhydroxylamine with aniline.

3.4. *Catalyst activity results*

The effect of increasing H^+ content in K-OMS-2 was studied by the condensation reaction of aniline with PHA to produce 2-ADPA. The results are shown in Table 2. H-K-OMS-2(2C) with the highest $\%H^+$ gave the highest selectivity for the *ortho* isomer. The results demonstrate a trend toward increased selectivity with increasing $\%H^+$ in the catalyst. The conversion with respect to PHA was 100% in all of the reactions carried out at 110 °C or higher.

4. Discussion

XRD patterns of K-OMS-2 and different H-K-OMS-2 are shown in Fig. 2. The structure of OMS-2 was conserved even after successive H^+ exchange treatments. The slight shift of peak positions to the left indicates a slight increase in tunnel size, which may be due to distortion in the tunnel from the H^+ ion exchange. The amount of K^+ cation in K-OMS-2 and in different H-K-OMS-2 was obtained from the EDAX analysis data, and the percentage of K^+ exchanged with H^+ was calculated. After four successive exchanges with 1 M HNO_3, 40% of the K^+ was exchanged with H^+, and after two successive exchanges with concentrated HNO_3, 50% of the K^+ was exchanged with H^+.

The condensation reaction between PHA and aniline proceeds via nitrinium ion ($C_6H_6NH^+$) formation in acidic conditions [7]. When the reactions were carried out with K-OMS-2, no reaction occurred, because no H^+ was present to form $C_6H_6NH^+$ or for the reaction to proceed (Fig. 5). But when K-OMS-2 was ion-exchanged with H^+, 2-ADPA was one of the products obtained. The H^+ present in the tunnel protonates PHA; with the loss of H_2O, $C_6H_6NH^+$ is formed, which reacts with aniline to form 2-ADPA. The intermediate product is $C_6H_6NH^+$, in which the positive charge is at the 2-position stabilized inside the OMS tunnel. H-K-OMS-2 has a very unique structure consisting of a negatively charged framework of MnO_6 and positively charged cations H^+ and K^+ in the tunnel. This unique feature of the catalyst helps stabilize the nitrinium ion intermediate.

The positive charge on nitrinium ion is stabilized by the negatively charged framework, and the positively charged H^+ helps stabilize the unshared pair of electrons on nitrogen in the nitrinium ion. The nitrinium ion, in which the positive charge is at the 2-position, is suitably placed inside the tunnel for stabilization, but in the case of positive charge at the 4-position, the distance between nitrogen and the positive charge is about 4.74 Å, making its stabilization difficult. Because the positive charge at the 2-position in the intermediate is more stabilized than the 4-position, the nucleophile aniline attacks at the 2-position, resulting in predominantly 2-ADPA. As the percentage of H^+ exchange increases in K-OMS-2, the selectivity of the *ortho* ADPA increases. This may be due to the slight increase in the tunnel size due to the ion exchange, as evidenced by the XRD patterns, producing greater stabilization of the nitrinium ion intermediate in the tunnels of H-K-OMS-2 and leading to the formation of the *ortho* isomer of ADPA. All other solid acids as reported by Smith et al. give predominantly the *para* product [7]. The exact mechanism of the stabilization of the nitrinium ion intermediate inside the tunnel remains a topic for further investigation. It can be concluded that it must be the unique geometry of the tunnel of H-K-OMS-2 that stabilizes the intermediate nitrinium ion with positive charge on the *ortho* position. This argument is bolstered by the fact that all other solid acids and Bronsted acids give rise to the more stable *para* isomer.

Earlier studies by Post et al. on cryptomelane showed that cryptomelane's tetragonal geometry distorts to monoclinic when the ratio of the lattice Mn ionic radius to the tunnel cationic radius exceeds 0.48 [16]. This transition puts strain on the lattice, which in turn strains the Mn–O bonds. This strain is created because the ionic radius of H^+ is much smaller than that of K^+, which satisfies the condition for strain. The tetragonal to monoclinic transition also results in an increase in the number of Mn^{3+} sites, as was reported by Makwana et al. [17]. This is due to the larger ionic radius of Mn^{3+} compared with Mn^{4+}, which fits better in a monoclinic environment. The tunnel cation exchange increases the number of Mn^{3+} sites, which decreases the AOS of Mn, as evidenced by the decreased AOS of Mn with increasing $\%H^+$ in the tunnel. The strain on the Mn–O bond makes the negatively charged oxygen more available to stabilize the nitrinium intermediate, in which the positive charge is at the 2-position. This corroborates the proposed theory that an increased $\%H^+$ in the tunnel increases the selectivity of the *ortho* isomer of ADPA.

The effect of temperature on the reaction was studied by varying the temperature between 110 and 160 °C. The formation of the *ortho* product was more favorable at lower temperatures than at higher temperatures. As the temperature increases, *ortho* selectivity decreases. This is because the *ortho* isomer is the thermodynamically more stable product, whereas the *para* isomer is the more kinetically stabilized product, and so the selectivity of the *ortho* isomer increases at lower temperatures. Some of the PHA remained unreacted below 110 °C; thus, the best temperature for this reaction is 110 °C. The amount of catalyst did not have much effect on selectivity; varying the amount of catalyst from 0.2 to 0.5 g had no effect on the *ortho* selectivity.

5. Conclusion

Cryptomelane-type manganese oxides (OMS-2) were modified by exchanging K^+ tunnel cations with H^+. Successive exchanges with HNO_3 resulted in better H^+-exchanged material. These materials were used for the condensation reaction of phenylhydroxylamine with aniline. H-K-OMS-2-catalyzed reactions gave higher selectivity for 2-ADPA than for 4-ADPA. The reaction is a simple one-step process and is completed in only 35 min. H-K-OMS-2 is a unique catalyst that gives predominantly the *ortho* isomer. To the best of our knowledge, this is the only catalyst that yields the *ortho* isomer with high selectivity compared with the *para* isomer.

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