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The effect of the catalyst on the synthesis of 2,2′-dichlorohydrazobenzene during the electrochemical reduction of *o*-chloronitrobenzene

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ABSTRACT

In this paper, 2,2′-dichlorohydrazobenzene was synthesized by the electrochemical reduction of *o*-chloronitrobenzene using the ion-exchange membrane method. The effects of different catalysts (litharge, lead tetroxide, and lead nitrate) on the synthesis were investigated. The influence of different catalyst loading approaches on the electrochemical reduction were also examined. The structure and surface morphology of the catalysts were characterized by X-ray diffraction and scanning electron microscopy. Catalyst activity was examined by dynamic potential analyses and cyclic voltammetry. Litharge was found to induce the greatest improvement in the electrolysis reaction rate and also decreases the reaction time. Coating the catalyst on the cathode helps enhance the product yield. The possible reaction mechanism was studied, and the catalyst was found to play a key role in transforming raw substances into intermediates. However, there is little effect on intermediate product transformation into the desired product.

1. Introduction

2,2′-Dichlorohydrazobenzene (DHB) can undergo intramolecular rearrangement to produce 3,3′-dichlorobenzidine (DCB) in acidic medium. DCB is the intermediate for a series of yellow pigments such as benzidine yellow, benzidine yellow G, and permanent yellow HR, among others. This series accounts for about 25% of all organic pigments, resulting in increased attention directed towards the efficient production of DHB. Methods for DHB synthesis, such as metal-acid reduction, hydration-hydrazine reduction, catalytic hydrogenation and electro-chemical reduction have been reported in many papers [1]. Due to environmental pollution, laboriousness, and low yield, metal-acid reduction and hydration-hydrazine reduction are no longer performed. Catalytic hydrogenation reduction has a high yield but proceeds under harsh reaction conditions and requires expensive catalysts.

Electrochemical reduction based on ion-exchange membranes for the synthesis of DHB was first reported in the 1980s [2]. Although the yield is only 54%, this process has gradually become a research hotspot given its merits of environment friendliness, low cost, and mild reaction conditions. The use of electrons as the reducing agent has been called the “green chemosynthesis method.”

The electrochemical reduction of nitrobenzene has already been studied. Zuman [3] has proposed the mechanism of this reduction based on previous studies. Moglie [4] has examined the effect of reaction conditions on other groups when the nitro group of the aromatic nitrocompound is reduced. Different solid cathodes have also been used in the electrochemical reduction of nitrobenzene [5–10]. Very recently, our laboratory has developed a novel method of synthesizing DHB by electrochemical reduction. The influence of the cathodic surface morphology, electrolyte temperature, initial concentration, and volume ratio of *o*-chloronitrobenzene (*o*-CNB) on the synthesis of DHB are investigated [11].

Reports on the mechanism of electrochemical reduction and technical conditions of synthesis are numerous. However, studies on catalyst function, which are very important in improving the product yield, restraining the by-product, and shortening the reaction time, are limited. In the current study, DHB was synthesized from *o*-CNB in a membrane-separated cell on a porous Ni/Fe composite electrode. The effect of different catalysts (litharge, lead tetroxide, and lead nitrate) on the electrochemical synthesis of DHB was investigated. The influences of different catalyst loading approaches on electrochemical reduction were also examined. Finally, a possible reaction mechanism was proposed.

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2. Experimental

2.1. Reagents and raw materials

o-CNB was obtained from Henan Kaipu Chemical Factory, China. Toluene, methanol, and sodium hydroxide were obtained from Beijing Chemical Reagent Corporation, China. The perfluorosulfonate membrane was homemade. The foam nickel and iron mesh were purchased from Changsha Liyuan Material Corporation, China. The pore size of foam nickel is 300–500 μm and the mesh size of iron mesh is 100 mesh, respectively.

2.2. Preparation of the electrode plate

The iron mesh was used as the skeleton of the cathode, and was combined with the foam nickel, fixed with the pressing machine, sealed by silicone adhesive, and solidified for use. The prepared electrode was moistened by deionized water, uniformly coated with the appropriate catalyst using a hairbrush, and then dried. The anode was made of porous stainless steel.

2.3. Construction of the electrolytic cell

Fig. 1 shows the schematic diagram of the electrolytic cell. The cell is comprised of three compartments separated by two cationic exchange membranes. The cathode compartment had a volume of 250 mL and was sandwiched between two 125 mL anode compartments. The anode plate was placed close to the anode compartment, and the cathode plate was placed close to the cathode compartment. The anode and cathode were isolated by the perfluorinated sulfonic acid ion exchange membrane. The electrolytic cell was sealed by silicone adhesive.

2.4. Experimental procedure

The electrode plate was pretreated. The anode was polished by sand paper, and then washed with muriatic acid and deionized water. The perfluorinated sulfonic acid ion exchange membrane was immersed in dilute alkali. The electrolytic cell was assembled on the prepared cathode plate. The anode and cathode compartments contained sodium hydroxide solution (25% and 5% w/w, respectively). The temperature-controlling equipment and stirring apparatus were connected. The electrode plates were activated at a consistent current of 1 A for 40 min. The solution containing *o*-CNB was added at suitable temperature, current, and stirring speed.

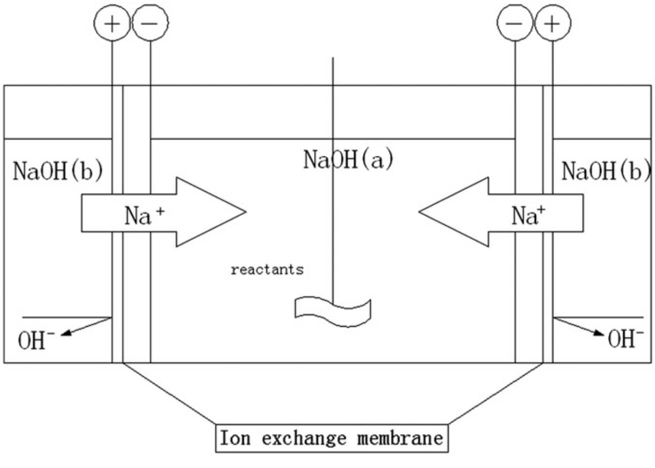


Fig. 1. Schematic view of the reaction unit.

2.5. Characterization

2.5.1. High-performance liquid chromatography (HPLC)

A HPLC system (Agilent 1200, Agilent, USA) was used to analyze the compositions of the cell (Fig. 2). The liquid chromatograph was equipped with a XBB-C18 column (250 mm × 4.6 mm, 5 μm) packed with silica gel. The mobile phase was composed of 75/25 (v/v) menthol/water at a flow rate of 1.0 mL/min. The wavelength used in the HPLC measurements was 220 nm. Different substances corresponded to different retention times, i.e., *o*-chloroaniline (*o*-CA) at 2.207 min, *o*-CNB at 2.555 min, toluene at 4.058 min, 2,2′-dichloroazoxybenzene (DOB) at 5.024 min, DHB at 7.403 min, and 2,2′-dichloroazobenzene at 13.310 min.

2.5.2. X-ray diffraction (XRD)

XRD patterns were obtained using an X-ray diffractometer (D/Max2500, Rigaku, Japan) using Cu Kα radiation, performed in the 2θ range of 5°–90° at a scan rate of 10° min^{-1}.

2.5.3. Scanning electron microscopy (SEM)

The electrode surface was characterized using a scanning electron microscope (S-4700, Hitachi, Japan) with an acceleration voltage of 20 kV.

2.5.4. The electrochemical measurement

The dynamic potential analyses and cyclic voltammetry were realized using an electrochemical station (Zahner-Electrik, Kronach, Germany).

3. Results and discussion

3.1. Comparison of different substance reactions in the electrolytic cell under catalyzed and uncatalyzed conditions

Adding the appropriate catalyst helps improve the selectivity and yield of the reaction. The different reactions were compared using litharge which is lead mono-oxide (PbO) as catalyst at a constant current of 1.1 A/dm^2. Fig. 3 shows the content variations of the raw substance (*o*-CNB), intermediate (DOB), product (DHB), and by-product (*o*-CA) under catalyzed and uncatalyzed conditions. There were significant differences between the changes in all substances in the two systems. The content of *o*-CNB decreases slowly without catalyst (Fig. 3a), and half of the substrate remains after 4 h. However, no *o*-CNB remains after 4 h under the catalyzed conditions (Fig. 3b). The electrode efficiency decreases due to the adsorption of by-products in the absence of the catalyst. More by-products result in lower reaction rates. Fig. 3a shows that the content of intermediate DOB increases slowly due to by-product accumulation. There is little chance of accumulation of the by-product on the electrode in the catalyzed system; thus, few by-products are present after 3 h (Fig. 3b). The transformation of DOB into DHB is rapid and completes within 2 h.

3.2. Effects of different catalysts

The three different catalysts (litharge, lead tetroxide, and lead nitrate) were used to activate the cathode electrode in the electrochemical reduction of *o*-CNB. Fig. 4 shows the content variation of the product using three different catalysts. The content of DHB is more than 80% using the three catalysts, indicating that all of them can produce active substances to accelerate the reaction. Notably, the DHB content suddenly increases after 4 h because *o*-CNB has completely transformed into the intermediate DOB after 4 h, and DOB easily transforms into DHB. The transformation time of DOB catalyzed by litharge is shorter than that of lead tetroxide and lead

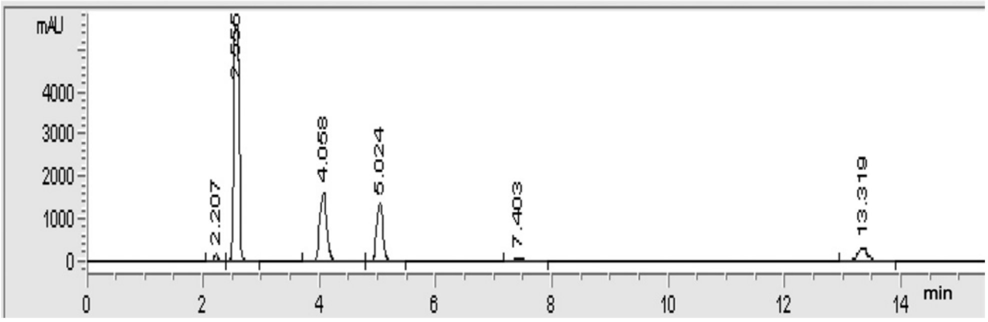


Fig. 2. HPLC chromatograms.

nitrate, and litharge produces the highest yield (95.17%). Fig. 5 shows the changes in the content of the by-product *o*-CA with time. According to the literature, *o*-CA is very difficult to transform into DHB, and gradually increases with the reaction once it emerges. The *o*-CA content catalyzed by litharge is lower than those catalyzed by lead tetroxide and lead nitrate, and does not exceed 5% in the end. Lead tetroxide and lead nitrate do not have sufficient catalytic activity at the beginning. As a result, the by-product *o*-CA is absorbed on the electrode, preventing *o*-CNB from making contact with the active hydrogen atoms and promptly transformed into DOB. Thus, the by-product content using lead tetroxide and lead nitrate are high.

The relationship between the activation potential and time was observed in the activation process of different catalysts (Fig. 6). The activation potential of litharge is the lowest among the three catalysts and remains stable. By contrast, the activation potentials

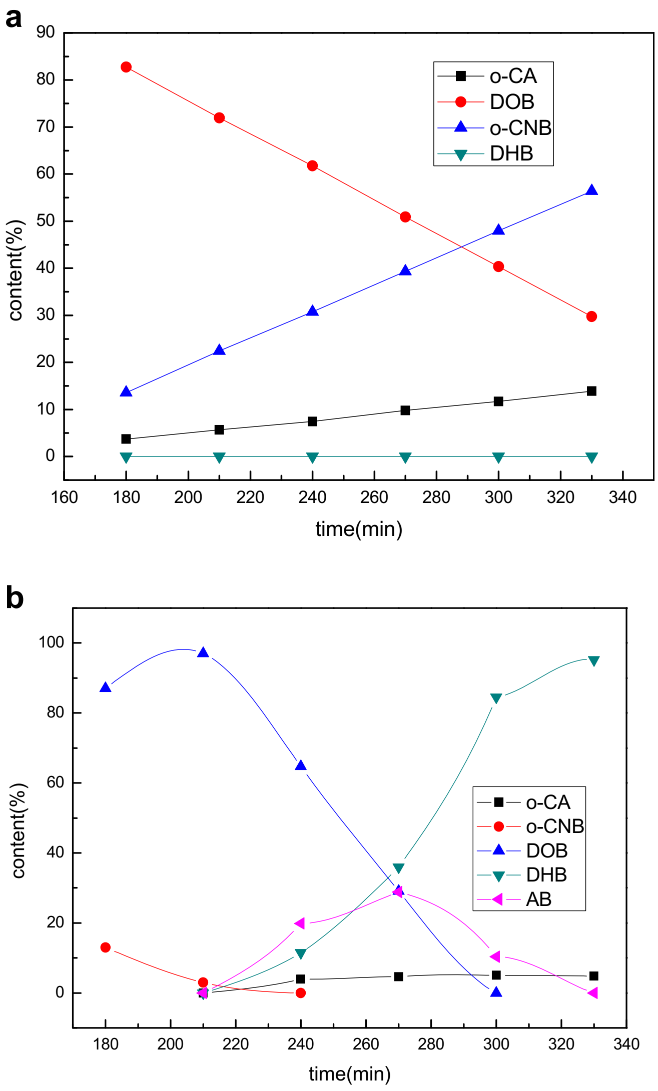


Fig. 3. The content variations of different substances (a) without and (b) with catalyst.

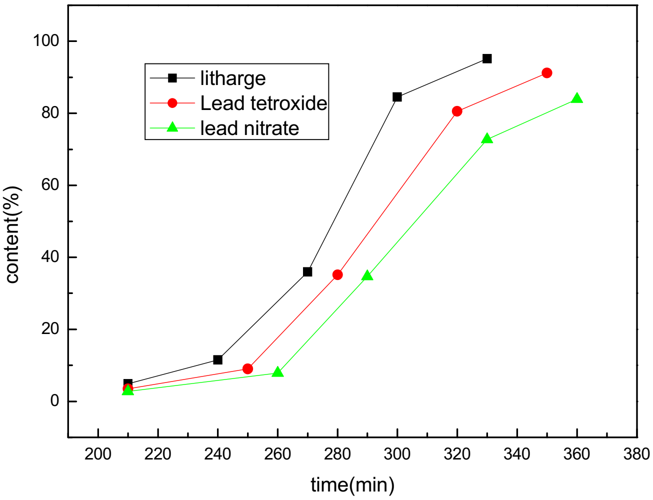


Fig. 4. The content variations of product using the different catalysts.

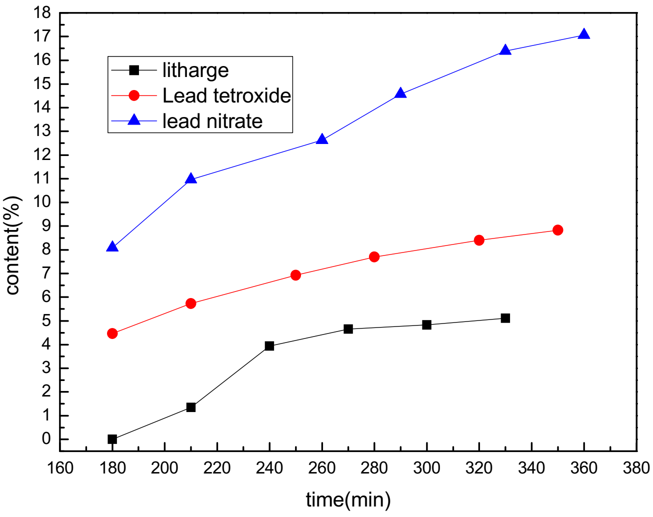


Fig. 5. The variations of by-product using the different catalysts.

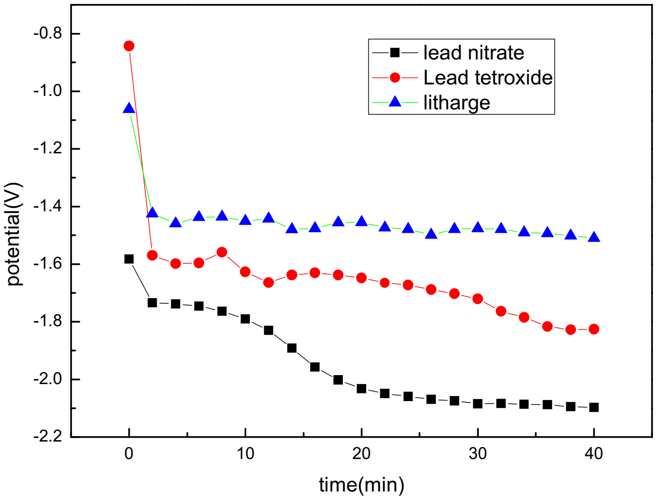


Fig. 6. The relationship between potential and the time in the activation process of different catalyst.

of lead tetroxide and lead nitrate greatly fluctuate, with that of lead nitrate reaching 2.1 V. The effects of lead tetroxide and lead nitrate on the chemical reaction are exerted during the activation process, resulting in higher potentials.

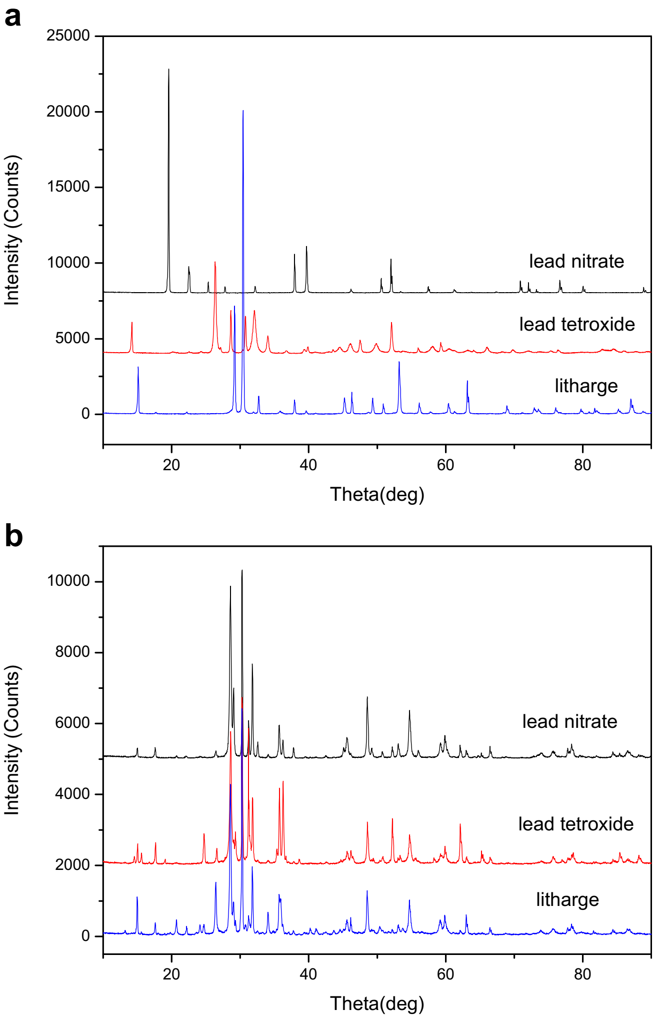


Fig. 7. The XRD graphs of different catalysts (a) before and (b) after activation.

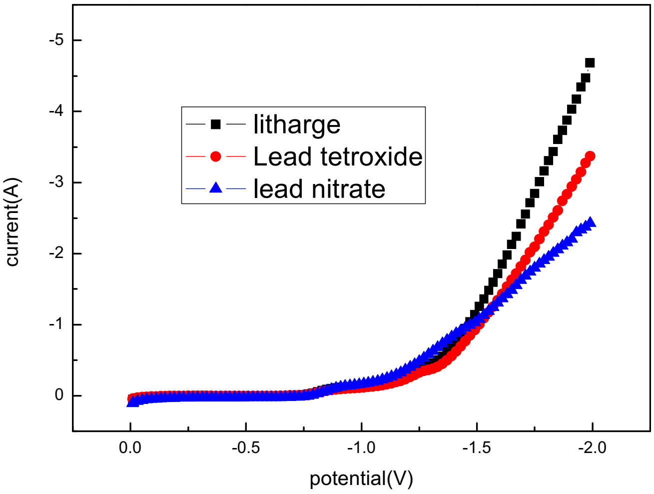


Fig. 8. Dynamic potential of electrode with different catalysts.

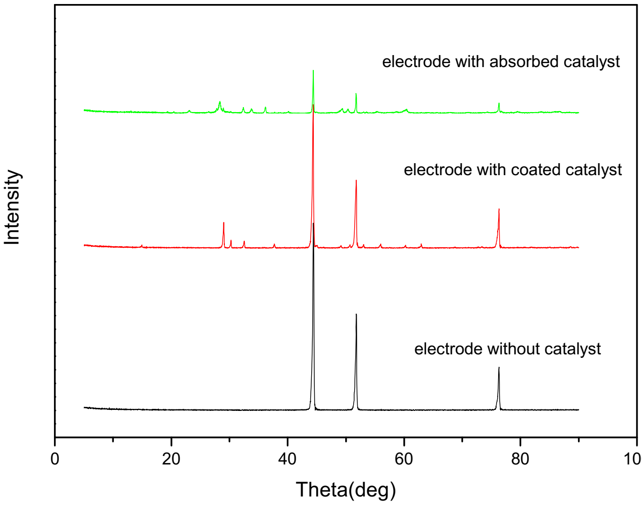


Fig. 9. XRD patterns of electrode plates at different loading method.

Fig. 7 compares XRD patterns of lead nitrate and lead tetroxide with that of litharge before and after activation by the electrochemical method. Litharge exhibits two strong peaks at 28.55° and 30.25° in Fig. 7a. The two peaks are characteristic of litharge.

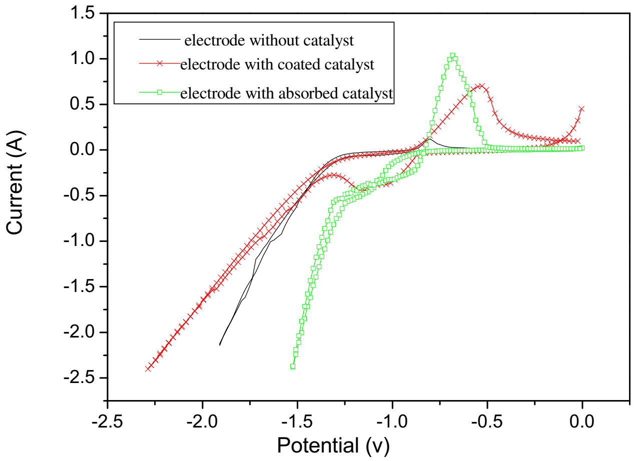


Fig. 10. CV curves of electrodes without catalyst, with coated catalyst and absorbed catalyst.

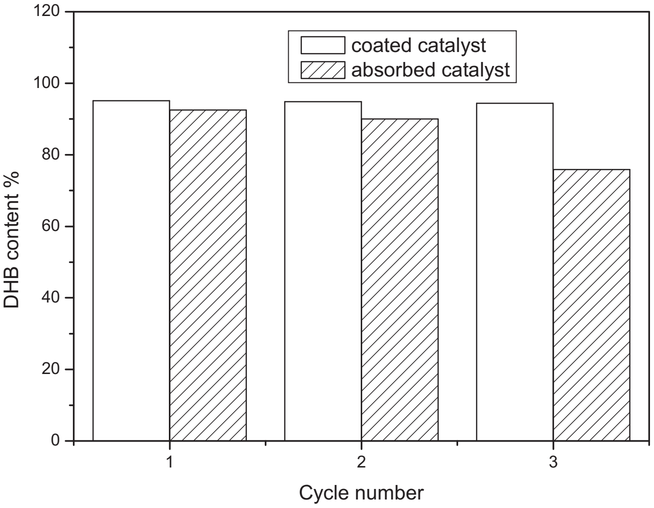


Fig. 11. DHB content variation using electrode with coated and absorbed catalyst at different cycle numbers.

Comparison with litharge diffractogram reveals that there is no litharge in lead nitrate, while lead tetroxide has litharge before activation, because lead tetroxide is comprised of litharge and lead dioxide. Fig. 7b shows all three curves exhibit two strong peaks at 28.55° and 30.25°, proving that numerous litharge molecules are present after the three catalysts are activated. The main active substance is litharge, which can explain why the catalytic activity of litharge is obviously higher than those of lead nitrate and lead tetroxide. Lead tetroxide has higher activity than lead nitrate. The reason is due to the existence of litharge in lead tetroxide before activation. Lead tetraoxide and lead nitrate are reduced in the cathode; they produce not only litharge but also other products such as lead. The equivalent catalysts produce unequal amounts of litharge after the activation, leading to the different catalytic effects.

The activity of the electrode coated by different catalysts was investigated by the dynamic potential method. The activated electrodes were used as the working electrodes, and porous stainless steel electrodes were used as the counter electrodes. The reference electrodes were saturated calomel electrodes. The

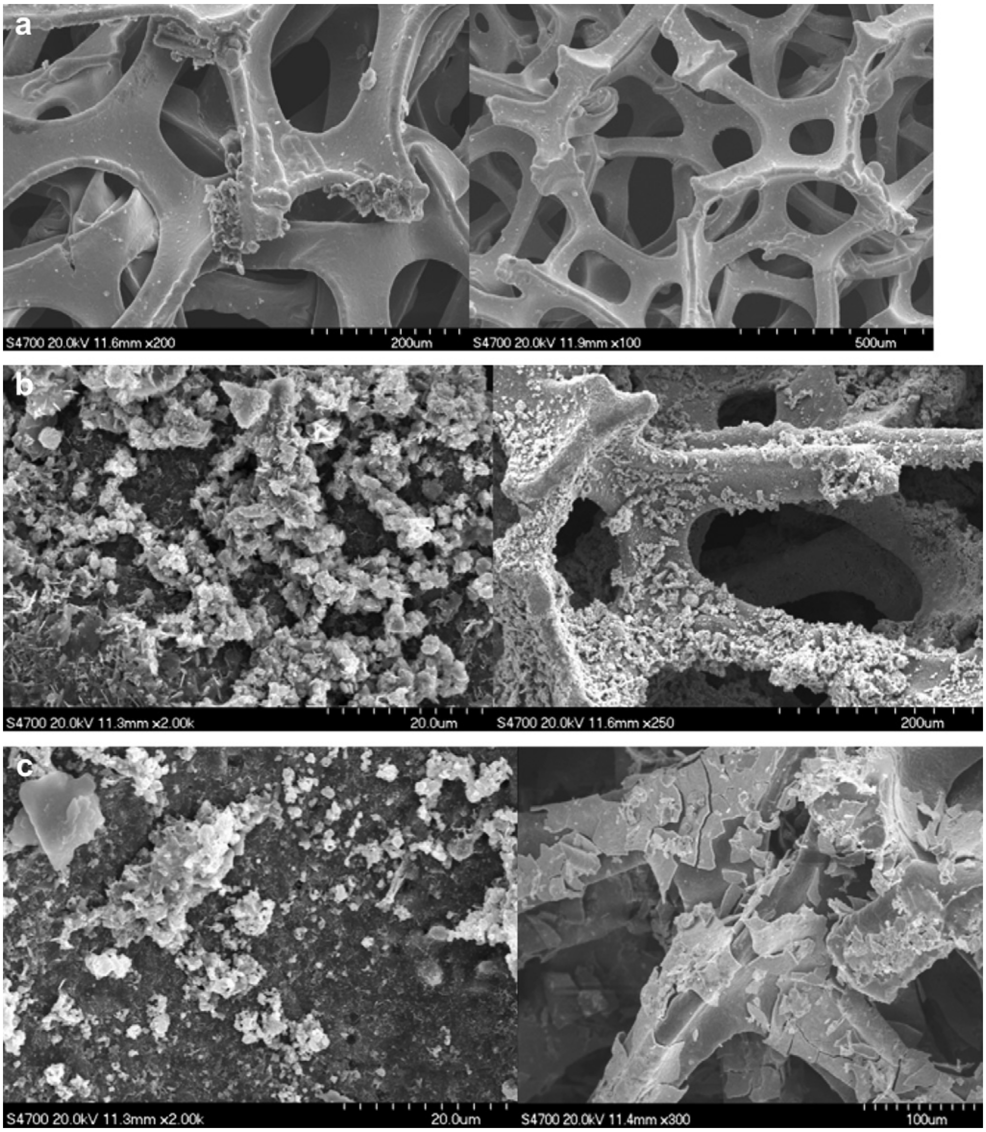
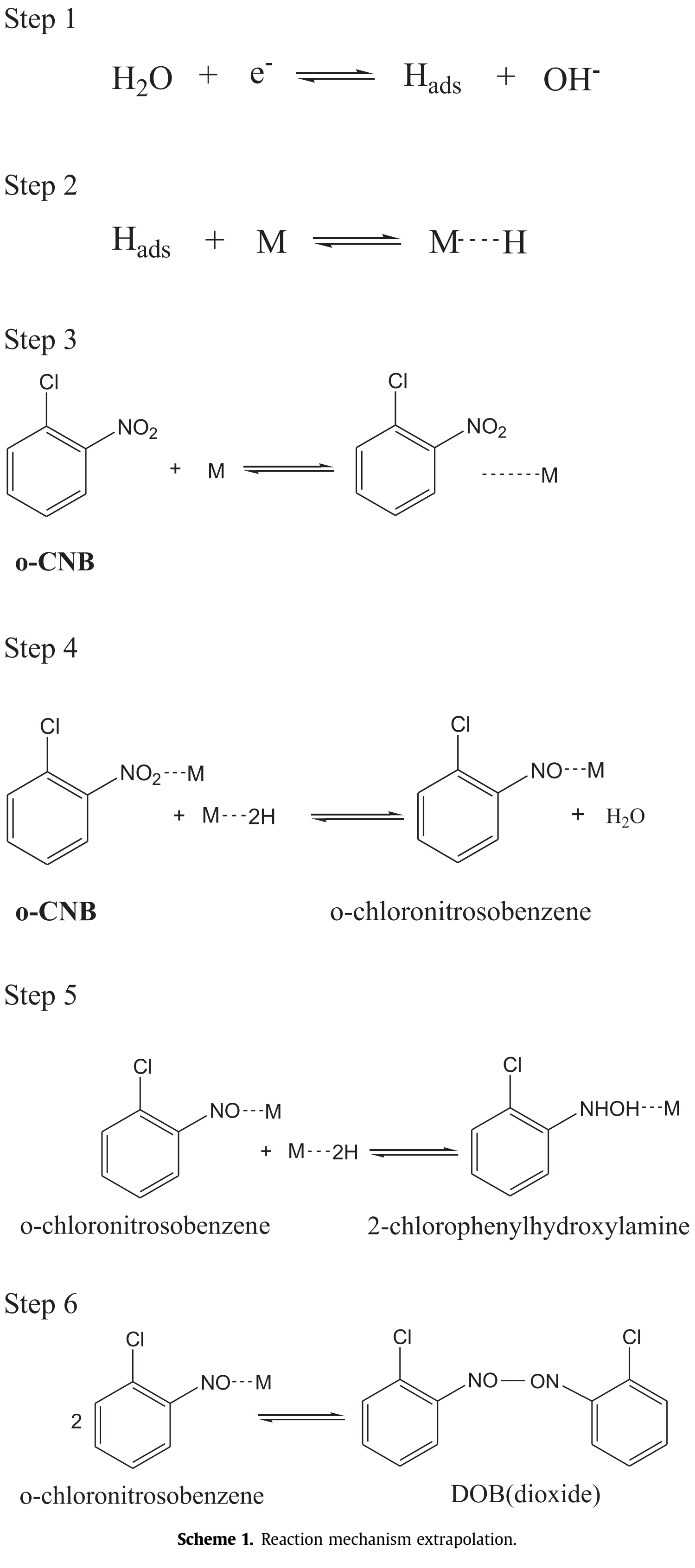
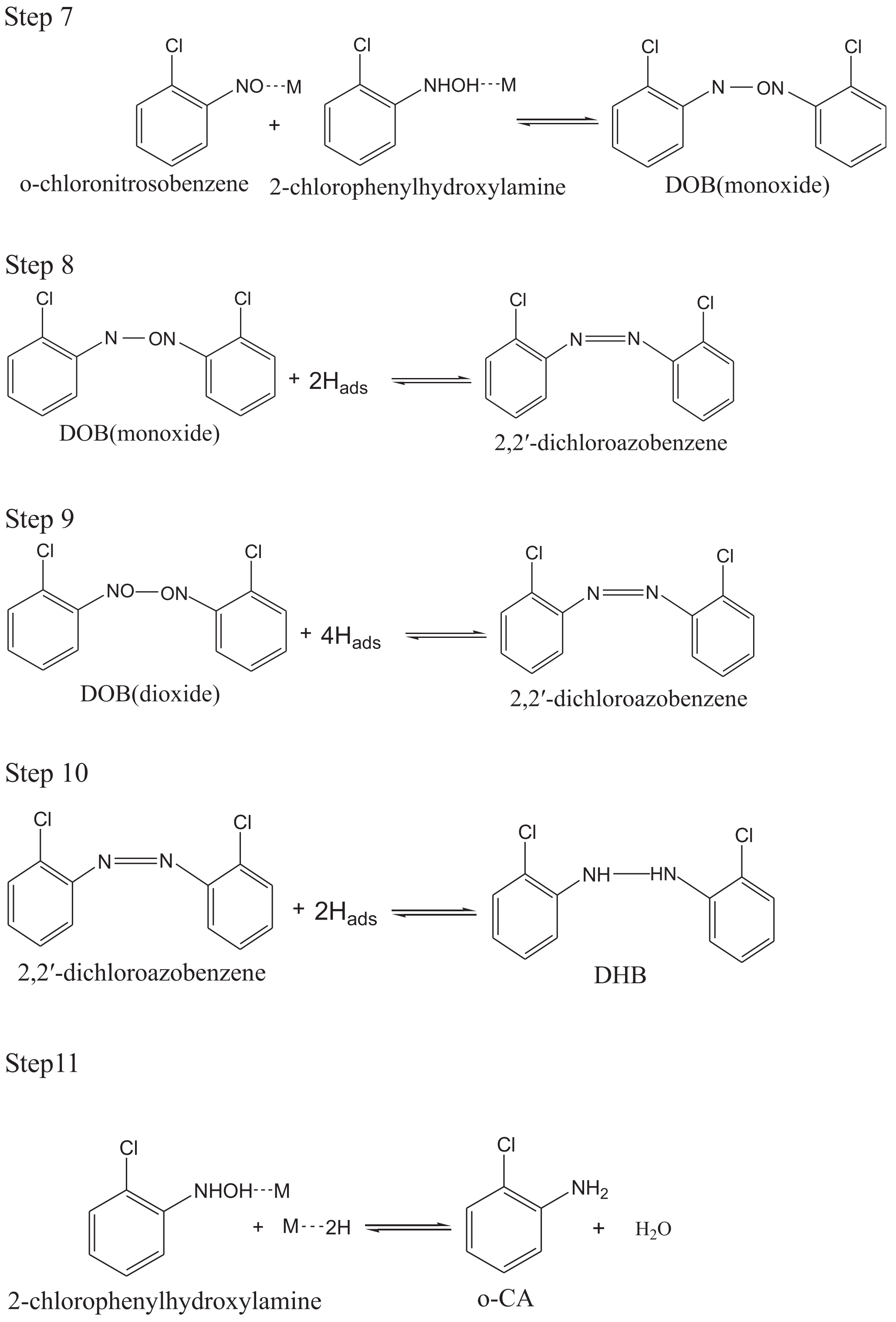


Fig. 12. SEM photographs of the electrode surface (a) without catalyst, (b) with coated catalyst and (c) absorbed catalyst.



Scheme 1. Reaction mechanism extrapolation.



Scheme 1. (*continued*).

highest scanning potential was −2 V and the scanning rate was 10 mV/s. The relationship between the activation potential and current is shown in Fig. 8. At the same potential, a higher current results in a better mass transfer effect, better electrode activity, and lower energy consumption. The current is almost unchanged with increased potential from 0 V to 0.8 V because of high membrane impedance in this phase. There is a linear increase in the current with increased potential beyond 1.2 V. Using litharge, the current remarkably increases. The results illustrate that activated litharge improves the electrode performance, which decreases the cell voltage under constant current electrolysis as reducing the energy consumption and improves the catalytic effect. Lead nitrate and lead tetraoxide consume some electrons for their self-reduction in the activated process, and the effect of mass transfer is reduced.

3.3. *Effect of the catalyst loading method*

The different loading methods of the catalyst litharge on the electrode were investigated while fixing the other technological conditions. The catalysts were evenly coated on nickel iron composite electrodes, and the electrolytic cell and electrolyte were prepared for the first group. In the second group, the same amount of catalyst was directly added to the cathode cell with the cathode electrolyte, and the catalyst was absorbed on the electrode surface after applying the voltage. The XRD patterns of the electrode plates at different loading modes are shown in Fig. 9. Litharge is successfully loaded on the electrode surface regardless of the coating or absorption method. The performance of the electrodes was determined by cyclic voltammetry (CV) at the scan rate of 10 mv/s (Fig. 10). The oxidation peak of the electrode with coated catalyst appears at a lower potential than that of the electrode with absorbed catalyst, proving that the coated catalyst can effectively decrease the reactive activation energy.

Fig. 11 shows that DHB productivity using the coated catalyst is higher than that using the absorbed catalyst. The coated catalyst has a shorter reaction time than the absorbed catalyst. Fig. 11 shows that DHB productivity gradually decreases with increased cycle numbers. The absorbed catalyst possibly falls off from the electrode surface after several cycles, thus affecting the catalytic effect, as also confirmed by SEM.

The SEM images of the electrode surface without catalyst as well as with coated and absorbed catalyst are shown in Fig. 12. Clearly, the electrode surface without catalyst is smooth (Fig. 12a). After activation by the coated catalyst, the electrode surface uniformly covers a layer of floccus (Fig. 12b). The coated catalyst tightly combines with the electrode and becomes difficult to remove even upon washing with organic solvent. The nickel iron composite electrode has a large specific surface, which provides the best site for the catalyst. The coated catalysts increase the amount of the active sites, thereby enabling the easy transformation of the substrate into the intermediate product and the reduced absorption of the by-product on the electrode. Ultimately, the yield of DHB is improved. The absorbed catalysts do not disperse well, cluster together, join loosely, and fall off easily (Fig. 12c). As a result, the DHB yield gradually decreases with increased cycle number.

3.4. *Reaction mechanism extrapolation*

Combined with the mechanism of the electrochemical reduction of nitrobenzene and the phenomena observed in the experiments, a possible reaction mechanism is presented in Scheme 1.

Electrodes are obtained from water electrolysis in the cathode cell solution, producing active hydrogen atoms (H_{ads}) and hydroxyl ions (step1). Active hydrogen atoms are adsorbed on the catalyst surface, and M represents an electrode surface with coated catalyst (step2). The sodium ions in the anode solution penetrate into the cathode through the ion exchange membrane to balance the hydroxyl ions, thereby improving the mass transfer efficiency. The raw substance *o*-CNB makes contact with active hydrogen atoms on the electrode surface, producing *o*-chloronitrosobenzene (step4), which that can combine with H_{ads} to produce 2-chlorophenylhydroxylamine (step5). The reaction intermediate 2,2′-dichloroazoxybenzene (monoxide and dioxide) can be produced from *o*-chloronitrosobenzene and further combine with each other and with 2-chlorophenylhydroxylamine (step6, 7). The reaction intermediate DOB continues to react with H_{ads} to produce 2,2′-dichloroazobenzene (step8, 9) and the product DHB (step10), whereas 2-chlorophenylhydroxylamine becomes the by-product *o*-chloroaniline (step11). Based on above mechanism, the catalyst plays a key role in the transformation of the raw substance into intermediates; however, the catalyst has little effect on the transformation of the intermediate into the desired product.

4. Conclusion

A catalyst plays an important role in DHB synthesis by the electrochemical reduction of *o*-CNB; it improves the transformation rate of the substrate and decreases the reaction time. By investigating the three kinds of catalysts, i.e., litharge, lead tetroxide, and lead nitrate, the main active substance in the electrochemical reduction is found to be litharge. The comparison of the catalyst loading method on the electrode reveals that coating the catalyst on the cathode can improve the DHB yield. A possible reaction mechanism is proposed. Based on this mechanism, the catalyst plays a key role in the transformation of the raw substance into intermediates, but not on the transformation of the intermediates into the desired product.

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