Mesoporous silica dispersed Co$_3$O$_4$-CuO nanocomposite and its catalytic reduction of 4-nitrophenol

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Keywords: mesoporous silica, hydrothermal, p-nitrophenol, catalytic reduction

Abstract

Herein, a catalyst Co$_3$O$_4$-CuO nanocomposite uniformly dispersed on mesoporous silica nanospheres (MSN) has been successfully synthesized through hydrothermal method. The synthesis method is simple and convenient, the prepared Co$_3$O$_4$-CuO nanocomposites have high dispersibility, and the support SiO$_2$ maintains the structure of mesoporous nanospheres. What’s more, the porous structure enables the obtained composite to have a high specific surface area (128.89 m$^2$ g$^{-1}$), which is easier to be contacted by catalytic substrates. The catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was investigated. The results show that the nanocomposite catalyst Co$_3$O$_4$-CuO@MSN present good catalytic performance, which can completely convert 4-NP to 4-AP in 200 s and the reaction rate constant $k$ is up to 0.149 s$^{-1}$. More important, the possible degradation mechanism was also proposed in the paper.

1. Introduction

Water pollution is the main environmental problem faced by today’s society, in which 4-nitrophenol (4-NP) is one of the most toxic and refractory organic pollutants and difficult to be removed due to its stability against chemical and biological degradation [1–5]. Recently, different techniques have been developed for the removal of 4-NP pollutants, such as adsorption, membrane filtration, catalytic degradation and so on [6]. To date, the direct catalytic reduction of 4-NP to 4-aminophenol (4-AP) is becoming an important route, because 4-AP has a great importance in the pharmacy and dyeing industry as a potent intermediate [7, 8]. Many reports are available on the reduction of 4-NP by noble metal nanoparticles as a catalyst [9–12]. However, noble metal nanoparticles are expensive and need organic polymers as a capping agent to prevent aggregation [13]. Therefore, to further optimize the composition and structure of catalyst is the focus of current research [14, 15].

Transition metal oxides (such as Co$_3$O$_4$, CuO, Fe$_3$O$_4$, etc.) with empty electron orbitals can accept and transfer electrons to form relatively stable complexes for rapid reaction, so they are widely used in various catalytic fields. Because the structure of single component oxides is relatively simple, two-component and multi-component composite oxides have been studied intensively due to their synergistic effects. For example, Chinnappan et al [16] synthesized three-dimensional flower-like Co$_3$O$_4$/NiO microspheres for the reduction of 4-NP. Li et al [17] prepared CuO-Co$_3$O$_4$@CeO$_2$ nanoparticles as heterogeneous catalysts by sol-gel method exhibited high catalytic performance. In addition, the existence of multivalent atoms and oxygen vacancies formed by the valence change can promote the hydrolysis of reducing agent NaBH$_4$ and the adsorption of $-$NO$_2$, thus, it can be used as a catalytic active site for the reduction of 4-NP [18, 19].

Mesoporous silica is widely used in various fields such as drug delivery [20–22], adsorption and separation [23, 24], and heterogeneous catalysts [25–29], due to its stable physicochemical properties, non-toxicity, low cost, high specific surface area, high pore volume, easy surface modification, good adsorption capacity and continuously adjustable pore size, etc. So as a support for metal oxides, mesoporous silica is an excellent...
candidate. Therefore, based on the advantages of transition metal oxides and mesoporous silica, nanocomposite metal oxides were designed to be uniformly dispersed by mesoporous silica with high specific surface area, which is expected to obtain catalysts with high catalytic activity and good stability for the reduction of 4-NP to 4-AP.

In this work, we successfully synthesized mesoporous silica nanospheres (MSN) dispersed nanocatalyst Co$_3$O$_4$-CuO by hydrothermal method, in which the Co$_3$O$_4$-CuO nanocomposite had high dispersibility and the support SiO$_2$ maintained the structure of mesoporous nanospheres. Furthermore, the obtained composite nanomaterial Co$_3$O$_4$-CuO@MSN was tested as a catalyst for the catalytic reduction of 4-NP, and its catalytic performance depends on its structure.

2. Experiment section

2.1. Chemicals
Cetyltrimethylammonium bromide (CTAB, 99%), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O, 99%), anhydrous copper chloride (CuCl$_2$, 98%), sodium hydroxide (NaOH, 96%) and Sodium borohydride (NaBH$_4$, 95%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China), 1, 3, 5-Trimethylbenzene (TMB, 98%) and Tetraethyl orthosilicate (TEOS, 98%) were obtained from Shanghai Merrill Chemical Technology Co. Ltd. (China), P-nitrophenol (4-NP) was purchased from Shanghai Gaoxin Chemical Glass Instrument Co. Ltd. (China). All the reagents were used without further purification.

2.2. Preparation of Co$_3$O$_4$-CuO@MSN composite catalyst
As shown in figure 1, the composite catalyst was prepared by the precipitation method. 2.9860 g of CTAB and 150 ml of deionized water were mixed in the beaker and sonicated for 20 min. It was then magnetically stirred at room temperature and the pH was adjusted to 10 with NaOH solution (2 M). After 15 min of reaction, 2.6770 g of CoCl$_2$·6H$_2$O and 0.5063 g of anhydrous CuCl$_2$ were added to the above solution, followed by continuing the reaction for 30 min. Then, 8.91 ml of TMB was dripped slowly into the beaker to promote the reaction for 15 min. After that, 11.2 ml of TEOS was trickled slowly into the beaker. After the reaction was continued for 24 h, all the suspension in the beaker was moved into a Teflon-lined stainless steel autoclave, which was placed in a blast drying oven at 120 °C for 6 h. Finally, the product was centrifuged (8000 rpm, 5 min), washed with deionized water and absolute ethanol alternately. After the above operation was repeated 3 times, the centrifuged precipitate was vacuum-dried at 60 °C. The dried solid was passed through a 100 μm sieve and then calcined at 550 °C for 6 h to obtain the composite catalyst Co$_3$O$_4$-CuO@MSN.
2.3. Characterization

The morphologies, structures and compositions of all samples were characterized by Field-emission scanning electron microscopy (SEM, ZEISS, GeminiSEM 300) and fully automatic surface and porosity analyzer (BET, McMurray, Mc2460). Powder x-ray diffraction (XRD) patterns were carried out on a Bruker D8 Focus diffractometer (German) with Cu Kα radiation source (λ = 0.1541 Å) at 40 kV, 40 mA. Element type and composition were obtained by using x-ray Photoelectron Spectroscopy Analyzer (XPS, THERMO, NEXSA).

2.4. Catalytic degradation of p-nitrophenol

50 ml of the previously prepared 4-NP (0.1 MM) solution and 2 ml of the prepared NaBH₄ (0.2 M) solution were mixed in the beaker. Then, 200 μl of the dispersed 0.1 g/l Co₃O₄-CuO@MSN composite catalyst was added to the above mixed solution. The beaker was placed on a magnetic stirrer for magnetic stirring. After that, samples were taken from the beaker every 50 s (0, 50, 100, 150, 200, 250 s). The collected samples were filtered to obtain the supernatant, which was placed in the sample tank of the UV spectrophotometer to judge the conversion of 4-NP by observing the absorption peak intensity of the sample at 400 nm.

3. Results and discussion

3.1. The morphology, structure and composition of Co₃O₄-CuO@MSN composite

The morphology and structure of Co₃O₄-CuO@MSN were shown in figure 2. It can be seen from SEM image (figures 2(A)-(B)) that metal oxides are evenly dispersed on the surface of MSN, which used CTAB as a template agent and TMB as pore expander. The Co₃O₄-CuO@MSN were characterized by XRD to obtain the crystal phase structure information of the composites. It can be seen from figure 2(C) that the diffraction peak of Co₃O₄-CuO@MSN are strong, sharp and no impurity. There are three distinct diffraction peaks at 35.5°, 58.4°, and 79.7°, corresponding to the (002), (202) and (023) crystal planes of CuO respectively, which consistent with
the standard card (PDF#80–1917). In addition, there are obvious diffraction peaks at 19°, 31.3°, 36.8°, 38.5°,
44.8°, 49°, 55.7°, 59.4°, 65.2°, 68.6°, which corresponds to (111), (220), (311), (222), (400), (331), (422), (511),
(440) and (531) facets of Co3O4, consistening with the standard card (PDF#74–2120). It shows that Co3O4 and
CuO have been successfully dispersed on the surface of MSN, proving that Co3O4-CuO@MSN composite has
been prepared. The characteristic peaks of MSN appear at 1–10°, and it can be seen from the small-angle x-ray
scattering (SAXS) pattern (figure 2(D)) that three diffraction crystal planes of MSN at (100), (110) and (200),
corresponding to three diffraction peaks at 2θ = 1.9°, 3.8° and 4.43°, respectively. This is consistent with MSM-
41-type mesoporous SiO2.

Figures 3(A) and (B) present the surface scanning element distribution map (Mapping) and EDS map of
the Co3O4-CuO@MSN composite catalyst, respectively. The distribution and content of each element of the
composite catalyst can be seen. It can be seen from figure 3(A) that the four elements O, Si, Co, and Cu are
uniformly distributed in the Co3O4-CuO@MSN composite catalyst. The characteristic peaks of the four
elements O, Si, Co, and Cu can be observed from figure 3(B). The above analyses reconfirm that the
Co3O4-CuO@MSN composite catalyst has been prepared successfully, and the metal oxides are uniformly
dispersed on the mesoporous silica support. According to the numerical data, the atomic percentages of Cu and
Co are 6.37% and 1.53% in the catalyst Co3O4-CuO@MSN, respectively.

The chemical valence and elemental composition of the Co3O4-CuO@MSN composite were analyzed by
XPS, and the results are shown in figure 4. It can be seen from figure 4(A) that there are four elements, O, Si, Co,
and Cu in the composite material, which are consistent with the EDS analysis results. In figure 4(B), the
magnified Cu 2p peak shows two peaks at 935.19 and 955.13 eV, resulting from the spin–orbit splitting of 2p3/2
and 2p1/2, respectively, which correspond to Cu2+. The two satellite peaks at 943.46 eV and 962.63 eV are the
vibrational peaks of high binding energy Cu. It can be shown from the figure 4(C) that a strong peak was found at
105.88 eV, corresponding to the characteristic peak of the Si 2p orbital in the Co3O4-CuO@MSN structure.
Furthermore, the strong peak at 533.8 eV corresponds to the lattice oxygen of the oxides in the composite as
shown in figure 4(D), and the oxygen in each oxide has the same chemical state. As shown in figure 4(E), there
are two salient peaks at the binding energies of 780.13 eV and 795.86 eV, corresponding to Co 2p3/2 and Co
2p1/2, respectively. The two Co 2p3/2 peaks at 779.52 eV and 781.38 eV are attributed to Co (III) and Co (II),
and the two Co 2p1/2 peaks at 797.87 eV and 796.86 eV are attributed to Co (III) and Co (II), respectively. Combined
with the two satellite peaks at 785.92 and 801.75 eV, the successful loading of Co3O4 was proved. Figure 4(F)
shows the XPS spectra of C 1 s in Co3O4-CuO@MSN. The peaks of C 1 s are about 284.76 eV and 286.67 eV,
which are related to the binding energies of C-C and C-OH, respectively [30, 31]. The above results demonstrate
that Co3O4-CuO@MSN has been successfully prepared, consistingent with the previous XRD test.

Figure 5 shows the nitrogen adsorption–desorption isotherms of MSN and Co3O4-CuO@MSN composites.
It can be observed from the figure 5 that the curves of MSN and Co3O4-CuO@MSN show the characteristics of
III-type isotherms, indicating that MSN and Co3O4-CuO@MSN have regular mesoporous structures, and the
prepared Co3O4-CuO@MSN did not destroy the structure of mesoporous silica, which is consistent with the
SEM characterization results. The adsorption and desorption branches can be calculated according to the
Barret-Joyner-Halenda model and the pore size distributions of MSNs and Co3O4-CuO@MSN can be obtained.

![Figure 3. Mapping(A) and EDS spectrum with elemental composition in the inset (B) of Co3O4-CuO@MSN nanocomposites.](image-url)
specific surface area, pore volume and pore size of Co3O4-CuO@MSN composites are lower than those of MSN due to Co3O4-CuO nanoparticles will block some of the pores. In general, Co3O4-CuO@MSN has a relatively high specific surface area, which is beneficial to the improvement of catalytic activity.

3.2. Catalytic performance of catalysts
When NaBH4 was added to the reaction system, the 4-NP solution changed from light yellow to yellow, accompanied by the generation of a large number of air bubbles, as shown in figure 6(A), indicating the formation of sodium 4-NP. At the same time, the UV absorption characteristic peaks from 317 nm to 400 nm (figure 6(B)). Therefore, the intensity of the peak at 400 nm can represent the concentration of the substrate 4-NP.

In order to test the catalytic activity of Co3O4-CuO@MSN composite, we explored its catalytic reduction performance of 4-NP at room temperature. To more intuitively see the advantages of Co3O4-CuO@MSN in catalytic reduction reaction, we also tested the catalytic reduction performance of the comparison material: Co3O4–CuO nanocomposites, and the obtained UV–vis absorption spectra are shown in figure 6. In the absence of catalyst, the absorption peak did not change. However, after adding the catalyst, the intensity of the
absorption peak at 400 nm was found to decrease, while a new absorption peak appeared at 300 nm, corresponding to 4-AP. As the catalytic reaction continued, it was found that the absorption peak at 400 nm decreased, while the absorption peak at 300 nm increased. When the reaction progressed to 200 s, the absorption peak of the solution with Co3O4-CuO@MSN at 400 nm disappeared (Figure 6(C)), and the absorption peak at 300 nm became the strongest. So far, the catalytic reaction is over, that is, 4-NP has been completely reduced to 4-AP. In contrast, the reaction catalyzed by Co3O4-CuO cannot be completely degraded, indicating that the Co3O4-CuO@MSN composite has better catalytic performance.

Figure 7(A) shows the catalytic activity of MSN, Co3O4-CuO and Co3O4-CuO@MSN on the reduction of 4-NP by NaBH4. It can be seen from Figure 7(A) that the conversion rate for the reduction of 4-NP by Co3O4-CuO@MSN composite has reached 99.3% at 150 s, while that of the Co3O4-CuO catalyst is only 58.2%. This is due to the large specific surface area of Co3O4-CuO@MSN, which facilitates the contact between reactants and the catalyst, and significantly improves the activity of the catalyst. As a comparison, the catalytic activity of MSN material was also tested. It can be seen that the 4-NP concentration is only slightly decreased, which may be due to the physisorption of the MSN mesoporous structure. The amount of degradation (D%) of 4-NP was measured using the standard formula, namely D% = (A0 − At) / A0 × 100, where A0 represented the initial absorbance and At signified the absorbance at a time (t) [32]. The degradation rates of 4-NP corresponding to the catalysts Co3O4-CuO@MSN and Co3O4-CuO were 99.8% and 69.3%, respectively.

Kinetic analysis of the catalytic reactions of MSN, Co3O4-CuO and Co3O4-CuO@MSN was carried out. Figure 7B shows the kinetic curves of the catalytic reduction of 4-NP by MSN, Co3O4-CuO and Co3O4-CuO@MSN. In the whole catalytic system, due to the large excess of NaBH4 added, the concentration of BH4⁻ can be considered to be constant during the reaction. Therefore, the catalytic reduction of 4-NP is equivalent to a pseudo-first-order reaction. As can be seen from figure 7, the fitted ln(c_t/c_0) has a linear relationship with time t, indicating that the reduction of 4-NP by NaBH4 is consistent with a first-order kinetic model: ln(c_t/c_0) = kt (where k is the rate constant). The reaction rate constants for the catalytic reduction of 4-NP by MSN, Co3O4-CuO and Co3O4-CuO@MSN are: 0.003 s⁻¹, 0.071 s⁻¹, 0.149 s⁻¹, respectively. The results show that the Co3O4-CuO@MSN composite has the fastest reaction kinetics and the best catalytic activity due to the structural and compositional advantages of the Co3O4-CuO@MSN composite.
For comparison, the catalytic activities of various metal-based materials for 4-NP hydrogenation at room temperature are listed in Table 1. By comparison, it can be found that Co3O4-CuO@MSN exhibits excellent catalytic activity. This may be because the composites use MSN as the carrier, which increases the contact area between the catalyst and the substrate. Meanwhile, in the catalytic reduction process, Co3O4-CuO and MSN exhibited a good synergistic effect.

### 3.3. Stability testing of catalysts

The stability and reusability of Co3O4-CuO@MSN are crucial for its practical application. Therefore, its recyclability was evaluated and the results are shown in Figure 8(A). It can be seen that Co3O4-CuO@MSN maintains excellent catalytic performance for the degradation of 4-NP during 10 cycles. For the 10th use, approximately 84% of the 4-NP was still degraded within 200 s. Furthermore, compared to fresh catalysts, no obvious changes were observed in and SEM images (Figure 8(B)), XRD pattern (Figure 8(C)) and XPS survey scans (figure 4) of the used Co3O4-CuO@MSN. All the results clearly demonstrate the excellent stability of Co3O4-CuO@MSN in the catalytic degradation of 4-NP.

Based on the above series of characterizations and analysis of catalytic test results, the mechanism of catalytic reduction of 4-NP by Co3O4-CuO@MSN structure was studied (Figure 9). For heterogeneous catalytic systems, the catalytic reaction usually occurs on the surface of the catalyst, so the catalytic activity of the catalyst is largely determined by its surface structure [45, 46]. In the reaction system of catalytic reduction of 4-NP, after adding NaBH4, 4-NP was converted into sodium p-nitrophenolate ions adsorbed on the surface of Co3O4-CuO nanoparticles. Under the catalysis of Co3O4-CuO particles, the BH4⁻ ions are fragmented to generate active hydrogen species and bind to the surface of Co3O4-CuO nanoparticles. The adsorbed sodium p-nitrophenolate ions are reduced by these active hydrogens to give the final 4-AP [47, 48].
Figure 8. Catalytic cycling of 4-NP reduction by Co$_3$O$_4$-CuO@MSN (A). SEM image (B) and XRD pattern (C) of Co$_3$O$_4$-CuO@MSN nanocomposites after the 10th catalysis.

Figure 9. Catalytic mechanism of Co$_3$O$_4$-CuO@MSN reduction of 4-NP.
4. Conclusions

In this work, mesoporous silica was used as the support to disperse nanocomposite metal oxide catalysts, which have large specific surface area and abundant catalytic active sites, which effectively improves the catalytic reaction activity. The synthesized Co₃O₄-CuO @MSN composite can completely convert 4-NP to 4-AP in 200 s and the reaction rate constant k is up to 0.149 s⁻¹. This work provides meaningful guidance for the catalytic conversion application of 4-NP.

Acknowledgments

Authors are gratefully thankful to Fund of Visiting Scholar Fund of the State Key Laboratory of Silicon Materials (SKL2020–04), State Key Lab of Advanced Metals and Materials (2020–Z02), State Key Laboratory of Urban Water Resources & Environment, Harbin Institute of Technology (HCK202113), Key Laboratory of Advanced Materials of Ministry of Education (ADV21–6), State Key Laboratory of Crystal Materials, Shandong University (KF2109), State Key Laboratory of advanced refractory materials (SKLR202206), Shanghai Sailing Program (21YF1446800) by China for support.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare that there is no conflict of interest.

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