

Magnetic Recyclable Cu/ZnFe₂O₄ for Catalytic Reduction of Nitroarenes And C-N Bond Formation Reactions

Ruike Zhang

Northeastern University

Tian Chen

Northeastern University

Gongshu Wang

Northeastern University

Yuqiu Guan

Northeastern University

Guiyang Yan

Normal University

zhangpei chen (✉ chenzhangpei@main.neu.edu.cn)

Northeastern University

Jianshe Hu

Northeastern University

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Abstract

A magnetic recyclable Cu/ZnFe₂O₄ composite material was successfully prepared with cheap and easy-to-obtain raw materials. This obtained copper composite material could be employed as efficient catalyst for both degradation of aromatic nitro compounds and C-N bond formation reactions without extra ligands. The aromatic nitro compounds were reduced within 2 min with low catalyst dosage. And high catalytic activity, broad substrate scope and low loading were achieved for Ullmann-type C-N bond formation reaction. The morphology of Cu/ZnFe₂O₄ was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Energy disperse spectroscopy (EDS), Transmission electronic microscopy (TEM) and Scanning electron microscopy (SEM). In addition, this environmentally friendly heterogeneous catalyst could simply be recovered via magnetic decantation and used again for six cycles with no considerable loss in activity. This developed magnetic recyclable Cu/ZnFe₂O₄ composite had the characteristics of easy availability, high catalytic performance, good reusability good stability and magnetic recovery properties.

1. Introduction

Aromatic nitro compounds which are released from organic or textile industries, have been threatening both environmental safety and human health in recent years. Among them, the p-nitrophenol (p-NP) has been listed as priority toxic pollutants and hazardous wastes by United States Environmental Protection Agency [1]. Therefore, removal or degradation of such toxic compounds from waste water is of great significance. Till date, several methods including electrochemical oxidation [2], adsorption [3], biodegradation [4], and photocatalysis degradation [5] have been developed and applied to this research field. In particular, the catalytic reduction of nitroaromatic compounds to the corresponding amino compounds is considered one of the most efficient method because the generated amino compounds are important intermediates in the preparation of various useful products such as dyes, agricultural and pharmaceutical products [6].

The *N*-aryl nitrogen-containing heterocycles are valuable compounds that are present in numerous bioactive natural products, synthetic drugs, and materials [7]. Accordingly, the prevalence of these compounds have expedited the exploration of efficient and environmentally benign synthetic methods for their preparation. In this context, the copper-catalyzed Ullmann-type C-N bond formation reactions [8] that enable the coupling of aryl halides with nitrogen-containing compounds representing a straightforward, inexpensive approach to such compounds and have received high priority in synthetic community [9]. However, this copper-catalyzed synthesis usually confronts with some restrictions such as harsh conditions, stoichiometric dosage of copper, limited substrate scope, and reasonable to poor yields [10]. To overcome these drawbacks, researchers have employed several organic ligands and copper salts to facilitate this transformation [11]. In spite of the efficiency of these homogenous catalyst systems, due to the unrecyclable of the metal catalyst and the valuable ligands, together with the separation problems of the products expedited the fabrication of copper based heterogeneous catalysts for the C-N bond formation reaction. Anchoring appropriate ligands and copper to the surface of specially developed

supports is a viable strategy for the development of heterogeneous catalysts [12]. Several systems have been disclosed based on a series of recyclable supporting materials, such as hydroxyapatites [13], silica based materials [14], carbon nanotube materials [15], metal oxide materials [16], carbon nanotube materials [17], polymers [18] and metal oxide materials [19]. Despite much progress having been achieved in this research field, a great number of problems still remain unsettled, such as the extra synthesis steps for introduction of the ligands, agglomerate problems during the reaction process, reduced activity and reusability caused by the poor stability of the catalyst [20]. Therefore, the development of more efficient and easily available heterogeneous catalysts for the Ullmann-type C-N bond formation reactions is still highly desirable.

Zinc ferrite (ZnFe_2O_4) possesses large saturation magnetization and low coercivity which lead to its huge application prospects as magnetic recyclable materials [21]. Magnetic recyclable catalysts based on zinc ferrite avoiding filtering or centrifugal separation procedures would be a reliable solution for the separation problems in terms of heterogeneous Ullmann-type C-N bond formation reactions. However, the fabrication of available zinc ferrite-supported copper catalyst ($\text{Cu}/\text{ZnFe}_2\text{O}_4$) should settle the following intrinsic obstacles: 1) the difficulty of possessing both high catalytic activity and good magnetic properties because of the fact that the catalytic active copper is prone to be wrapped by the surrounding catalytically inactive magnetic materials; 2) the stability of the materials under reaction conditions, such as high temperature, pH, organic corrosion and so on; 3) issues associated with the catalytic activities and catalytic efficiency. Considering the importance of developing efficient heterogeneous catalysts for degradation of aromatic nitro compounds and C-N bond formation reactions, together with our continuous investigation on the application and development of magnetically recoverable materials [22], herein we wish to report a novel $\text{Cu}/\text{ZnFe}_2\text{O}_4$ composite material as efficient catalyst for both of the above mentioned reactions. This developed composite features easy availability, high catalytic performance, and good reusability via a simple magnetic separation method.

2. Experimental

2.1 Synthesis of $\text{Cu}/\text{ZnFe}_2\text{O}_4$ composite catalyst

The solution of $\text{Cu}(\text{NO}_2)_2$ (67 mmol) dissolved in 100 mL diethanolamine was heated slowly to 150 °C and stirred vigorously for 3 h in nitrogen atmosphere. The color of the mixture turned red as the reaction proceeds. After cool down to room temperature, copper precipitates were obtained by centrifugation. Then, a solution of FeCl_3 (9.5 mmol, 1.504 g) and ZnCl_2 (4.4 mmol, 0.600 g) in 100 mL deionized water was sonicated for 3 h at room temperature. Then, NaOH (3 M, 30 mL) was added into the mixture. And then the temperature of the ultrasonic water bath was raised to 60 °C for 1 h, finally magnetic suction out ZnFe_2O_4 . The obtained ZnFe_2O_4 was dispersed in 100 mL deionized water, and a mixture of the above obtained copper precipitate in 50 mL ethanol was added. And the resulting mixture was heated at 80 °C and agitated for 50 min. The solid precipitate was then separated with a magnetic bar and washed with

distilled water and anhydrous ethanol. Then the Cu/ZnFe₂O₄ composite was obtained after drying at 160 °C for 2 h.

2.2 Cu/ZnFe₂O₄ catalyzed reduction of p-nitrophenol

A mixture of p-nitrophenol (2 ml, 400 ppm), NaBH₄ and Cu/ZnFe₂O₄ (3–10 mg) was added to a quartz cuvette, and the reaction was monitored with an ultraviolet-visible spectrophotometer. At this time, the system turns from bright yellow to colorless.

2.3 Cu/ZnFe₂O₄ catalyzed C-N bond forming reactions

A mixture of Cu/ZnFe₂O₄ (100 mg, 4.8 mol%) and Cs₂CO₃ (0.6500 g, 2 mmol) was added to the re-sealable test tubes (25 mL) with Teflon septa. The tube was emptied and filled with nitrogen, then the process was repeated three times. EtOH (1.0 mL), **3a** (1.5 mmol, 0.3060 g) and **4a** (1.0 mmol, 0.0681 g) were added through a syringe under N₂, afterwards sealed the reaction tube. Heated the mixture at 120 °C for 12 h, and cool down to room temperature. The organic phase was extracted by CH₂Cl₂, then dried on anhydrous magnesium sulfate and concentrated by rotary evaporation. Finally, the crude product was purified by column chromatography (ethyl acetate: petroleum ether = 2:1) to afford **5a** (0.1356 g, 94% yield).

3. Results And Discussion

3.1 Characterization of the Cu/ZnFe₂O₄ catalyst

The Cu/ZnFe₂O₄ catalyst was synthesized by loading Cu species on zinc ferrite particles through ultrasound assisted co-precipitation (Supplementary data). The structure of the fabricated zinc ferrite and Cu/ZnFe₂O₄ materials were characterized by FT-IR, XRD, TGA, EDS, TEM and SEM.

As shown in Fig. 1 (a), the absorption peak at 556 cm⁻¹ is attributed to the Fe-O vibration from the magnetic basement [23]. The peak near 3440 cm⁻¹ is related to the O-H stretching vibration of coordinated the hydroxyl groups and water molecules in the layers. The peak around 1630-1660 and 1383 cm⁻¹ maybe caused by another absorption band corresponding to the water deformation [24]. The absorption peak at 618 cm⁻¹ indicated the existence of copper nanoparticles [25]. The TGA curves of Cu/ZnFe₂O₄ and ZnFe₂O₄ were shown in Fig. 1 (b). The Cu/ZnFe₂O₄ and ZnFe₂O₄ showed a mass loss of 7%, which was attributed to the loss of adsorbed water on the sample surface. Furthermore, the mass loss of Cu/ZnFe₂O₄ and ZnFe₂O₄ was 2%, which was due to the loss of crystalline water bound within the sample. The mass of Cu/ZnFe₂O₄ catalyst does not decreased significantly at 700 °C, which indicates that the Cu/ZnFe₂O₄ catalyst had good thermal stability. The Fig. 1 (c) showed the XRD patterns of Cu/ZnFe₂O₄, Cu (PDF#03–1015) and ZnFe₂O₄ (PDF#01–1108). The position and relative intensity of the position and relative intensity of the peaks in the Cu/ZnFe₂O₄ of XRD pattern were consistent with the

standard XRD pattern of ZnFe_2O_4 and Cu, indicating that the crystal structure of ZnFe_2O_4 was maintained during Cu loading processes. As shown in Fig. 1 (d) the elemental composition was determined by EDS analysis and the results indicated the existence of O, Cu, Zn and Fe elements and further confirmed the structure of $\text{Cu}/\text{ZnFe}_2\text{O}_4$. The SEM and TEM images of the obtained catalysts were showed in Fig. 1 (e) (f) (g) (h). As shown, $\text{Cu}/\text{ZnFe}_2\text{O}_4$ and ZnFe_2O_4 were still irregular shape and nearly uniform size. The surface of ZnFe_2O_4 is changed after the introduction of Cu nanoparticles, and needle-like Cu single crystals are loaded on the original smooth surface.

3.2 Degradation of aromatic nitro compounds with $\text{Cu}/\text{ZnFe}_2\text{O}_4$

After investigation of the morphology of $\text{Cu}/\text{ZnFe}_2\text{O}_4$, we continue to study the catalytic performance of $\text{Cu}/\text{ZnFe}_2\text{O}_4$. The catalytic activity of $\text{Cu}/\text{ZnFe}_2\text{O}_4$ in the reduction process of p-nitrophenol to p-aminophenol was investigated with NaBH_4 as the reducing agent. Add p-nitrophenol (2 ml, 400 ppm), NaBH_4 and $\text{Cu}/\text{ZnFe}_2\text{O}_4$ (3mg, 5mg, 7mg, 10 mg) to the flask, and measure the data with an ultraviolet-visible spectrophotometer with a wavelength of 200-600 nm. The decrease in peak intensity at 400 nm is due to the reduction of p-nitrophenol. At this time, the stability of the peak intensity also indicates the proceeding of the reaction. Fig. 2 (a) depicted the UV spectra of the reduction of p-nitrophenol in terms of different reaction time. Fig. 2 (b) and (c) showed the kinetic experiments of the reduction reactions. As shown in formula (1), C_t is concentration of p-nitrophenol with the passage of time, and C_0 is concentration of p-acylphenol at the beginning of the reaction.

$$\ln(C_t/C_0) = kt \quad (1)$$

When the catalyst dosage is increased from 3 mg to 10 mg, the k value increased from $1.31 \times 10^{-2}/\text{s}$ to $4.02 \times 10^{-2}/\text{s}$, the time required for the complete reduction of p-nitrophenol also decreased from 330 s to 120 s. As the concentration increases, the reaction rate also increases. The rate of reaction depends on concentration of p-nitrophenol, which conforms to the characteristics of a quasi-first order reaction. These studies demonstrated that in the reduction of p-nitrophenol, the $\text{Cu}/\text{ZnFe}_2\text{O}_4$ exhibited good catalytic activity.

Subsequently, in order to further explore the application of this catalyst in the reduction of aromatic nitro compounds, an array of substrate scope experiments was carried out under the optimum reaction conditions. As shown in Fig. 2 (d), all of the investigated nitro aromatic compounds are reduced to the corresponding amino compounds with high yields (Supplementary data). A series of functional groups were well tolerated including halogen, hydroxyl, carboxyl, alkoxy groups. Notably, both of the two nitro groups of 1,3-dinitrobenzene substrate could be reduced to amino groups in this transformation in 98% yield.

3.3 $\text{Cu}/\text{ZnFe}_2\text{O}_4$ catalyzed C-N bond formation reactions

3.3.1 Optimization of C-N bond formation reaction conditions

To further estimate the application possibility of Cu/ZnFe₂O₄ in catalysis, the C-N bond formation reactions were further investigated with iodobenzene (3a) and imidazole (4a) as the model substrates. Table 1 shows the reaction condition optimization studies. Generally, the nitrogen-based ligands play significant roles in the interaction with metal centers and affect the efficiency of the catalyst system in the C-N bond formation reactions [26]. Therefore, we firstly screened some commercially available ligands on the reactivity, including 1,10-phenanthroline, p-toluenethiol, thioanisole, and proline (entries 1-4). To our delight, we found that the reaction proceeded well without any extra ligand and the yield reached 94% with Cs₂CO₃ as the base in ethanol at 120 °C (entry 5). To our disappointment, further screening the base failed to elevate the reaction yield, including K₂CO₃, NaOH, and KOH (entries 6-8). Increasing the catalyst dosage (entry 9), elevating the reaction temperature (entry 10), and prolonging the reaction time (entry 11) also failed to increase the yield. What's more, decreasing the temperature (entry 12) or shortening the reaction time (entry 13) the reactivity deteriorated dramatically. In addition, altering the ratio of **3a** and **4a** had almost no influence on the reactivity (entries 14-15). Hence the optimal conditions for this reaction were as follows: 100 mg of Cu/ZnFe₂O₄, 120 °C, 1.5 equiv. iodobenzene and 2.0 equiv. of Cs₂CO₃ were added to ethanol for 12 h.

3.3.2 Substrate scope and recyclability investigations

Under the optimal conditions, the substrate scope of aryl halides and nucleophilic reagents were investigated and the results were shown in Table 2. In general, various aryl halides were transformed into the coupling products with 50-94% yields. The functional groups including methyl, methoxy, nitro, cyanide, bromine and trifluoromethyl were tolerated in this reaction. Then the steric effects were investigated via the exploration of substrates bearing methyl group at different position of aryl iodides (entries 2-4). Results demonstrated that the reaction proceeded mildly and delivered the products with high yields. Subsequently, the electronic effects of p-phenyl substituents were conducted (entries 5-9). Substrates bearing both electron-donating groups and electron-withdrawing groups could be converted to the products in 83-89% yield. It is noteworthy that other nucleophiles such as (benzo)imidazoles, benzotriazoles, pyrazols, and pyrroles were also tolerated in this reaction resulting in the corresponding products with high yields (entries 10-15). In addition, transformations with arylamines and cyclic amines, such as 1-phenylpiperazine, morpholine, and piperidine were also viable and furnished the products in 60-94% yields (entries 14-20). In order to further exploration of the substrate scope, several aryl bromides were also subjected to this transformation and all of the reactions were happened stably in 50-74% yields (entries 21-27). Disappointingly, reaction with aryl chloride as the coupling agent generated the product with only 10% of yield (entry 28).

Since one of the key properties of our catalysts is the magnetic response, the recovery and reuse of catalysts were worth focusing on. We are pleased that the catalysts could be quickly and easily recovered from the product via an external magnetic field. The results show that the catalyst could be recovered quickly and easily in the reaction system and used continuously for 6 times without obvious loss of activity (Figure 3).

5. Conclusions

To sum up, a magnetic recoverable Cu/ZnFe₂O₄ composite material was successfully prepared and well characterized. This copper composite material performed well in the reduction of nitroaromatics to amino aromatics with sodium borohydride as the reductant. For the Ullmann-type C-N bond formation reactions, Cu/ZnFe₂O₄ could also exhibit good catalytic activity and delivering the corresponding *N*-aryl nitrogen-containing heterocycles products with good to excellent yields. What's more, this heterogeneous catalyst could be easily separated and reused for several consecutive times with a magnetic bar without significant loss of their catalytic efficiency. Further investigations on applications of this magnetic recyclable copper composite material are underway in our laboratory.

Declarations

Acknowledgments

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References

1. H. Pan, Y. Peng, X. Lu, J. He, L. He, C. Wang, F. Yue, H. Zhang, D. Zhou, Q. Xia, Well-constructed Ni@CN material derived from di-ligands Ni-MOF to catalyze mild hydrogenation of nitroarenes. *Mol. Catal.* **485**, 110838 (2020). <https://doi.org/10.1016/j.mcat.2020.110838>
2. S.A. Ture, V.B. Patil, C.V. Yelamaggad, R. Martínez-Máñez, V. Abbaraju, Understanding of mechanistic perspective in sensing of energetic nitro compounds through spectroscopic and electrochemical studies. *J. Appl. Polym. Sci.* **138**, 50776 (2021). <https://doi.org/10.1002/app.50776>
3. M. Nasrollahzadeh, M. Sajjadi, S. Irvani, R.S. Varma, Green-synthesized nanocatalysts and nanomaterials for water treatment: Current challenges and future perspectives. *J. Hazard. Mater.* **401**, 123401 (2021). <https://doi.org/10.1016/j.jhazmat.2020.123401>
4. Y. Wang, Y. Hou, Q. Wang, Y. Wang, The elucidation of the biodegradation of nitrobenzene and p-nitrophenol of nitroreductase from Antarctic psychrophile *Psychrobacter* sp. ANT206 under low temperature. *J. Hazard. Mater.* **413**, 125377 (2021). <https://doi.org/10.1016/j.jhazmat.2021.125377>
5. X. Pu, B. Zhang, Y. Su, Heterogeneous Photocatalysis in Microreactors for Efficient Reduction of Nitrobenzene to Aniline: Mechanisms and Energy Efficiency. *Chem Eng Technol.* **42**, 2146–2153 (2019). <https://doi.org/10.1002/ceat.201800735>
6. R. Hosseinzadeh, N. Aghili, M. Tajbakhsh, SBA-15 Immobilized Phenanthroline–Copper(I) Complex as a Recyclable Efficient Catalyst for *N*-Arylation of Amides and *N* – H Heterocycles with Aryl Halides. *Catal Lett.* **146**, 193–203 (2015). <https://doi.org/10.1007/s10562-015-1622-4>

7. R. Xiao, H. Zhao, M. Cai, MCM-41-immobilized bidentate nitrogen copper(I) complex: a highly efficient and recyclable catalyst for Buchwald N-arylation of indoles. *Tetrahedron Lett.* **69**, 5444–5450 (2013). <https://doi.org/10.1016/j.tet.2013.04.106>
8. S. Hemmati, S. Ahany Kamangar, M. Yousefi, M. Hashemi Salehi, M. Hekmati, Cu(I)-anchored polyvinyl alcohol coated-magnetic nanoparticles as heterogeneous nanocatalyst in Ullmann-type C–N coupling reactions. *Appl. Organomet. Chem.* **34**, e5611 (2020). <https://doi.org/10.1002/aoc.5611>
9. A.R. Sardarian, M. Kazemnejadi, M. Esmaeilpour, Functionalization of superparamagnetic Fe₃O₄@SiO₂ nanoparticles with a Cu(II) binuclear Schiff base complex as an efficient and reusable nanomagnetic catalyst for N-arylation of α -amino acids and nitrogen-containing heterocycles with aryl halides. *Appl. Organomet. Chem.* **35**, e6051 (2021). <https://doi.org/10.1002/aoc.6051>
10. S.H. Alelaiwi, J.R. McKee, One-Pot Synthesis of Aminated Benzo-Fused Heterocycles and N-Substituted Dibenzothiophenes via Copper-Catalyzed Ullmann Type Reaction. *ACS Omega.* **6**, 6009–6016 (2021). <https://doi.org/10.1021/acsomega.1c00414>
11. X. Zhao, Y. She, K. Fang, G. Li, CuCl-Catalyzed Ullmann-Type C–N Cross-Coupling Reaction of Carbazoles and 2-Bromopyridine Derivatives. *J. Org. Chem.* **82**, 1024–1033 (2017). <https://doi.org/10.1021/acs.joc.6b02595>
12. J.B. Fathima, A. Pugazhendhi, M. Oves, R. Venis, Synthesis of eco-friendly copper nanoparticles for augmentation of catalytic degradation of organic dyes. *J. Mol. Liq.* **260**, 1–8 (2018). <https://doi.org/10.1016/j.molliq.2018.03.033>
13. S. Hemmati, A. Naderi, M. Ghadermazi, H. Veisi, SiO₂-functionalized melamine-pyridine group-supported Cu(OAc)₂ as an efficient heterogeneous and recyclable nanocatalyst for the N-arylation of amines through Ullmann coupling reactions. *C. R. Chim.* **21**, 659–668 (2018). <https://doi.org/10.1016/j.crci.2018.03.002>
14. E. Akhavan, S. Hemmati, M. Hekmati, H. Veisi, CuCl heterogenized on metformine-modified multi walled carbon nanotubes as a recyclable nanocatalyst for Ullmann-type C–O and C–N coupling reactions. *New J Chem.* **42**, 2782–2789 (2018). <https://doi.org/10.1039/C7NJ03240D>
15. H. Veisi, Y. Metghalchi, M. Hekmati, S. Samadzadeh, CuI heterogenized on thiosemicarbazide modified-multi walled carbon nanotubes (thiosemicarbazide-MWCNTs-CuI): Novel heterogeneous and reusable nanocatalyst in the C-N Ullmann coupling reactions, *Appl. Organomet. Chem.* **31** (2017). <https://doi.org/10.1002/aoc.3676>
16. C. Bodhak, A. Kundu, A. Pramanik, An efficient and recyclable chitosan supported copper(II) heterogeneous catalyst for C–N cross coupling between aryl halides and aliphatic diamines. *Tetrahedron Lett.* **56**, 419–424 (2015). <https://doi.org/10.1016/j.tetlet.2014.11.120>
17. S. Anuradha, D.D. Kumari, Pathak, Synthesis and development of Chitosan anchored copper(II) Schiff base complexes as heterogeneous catalysts for N-arylation of amines. *Tetrahedron Lett.* **56**, 4135–4142 (2015). <https://doi.org/10.1016/j.tetlet.2015.05.049>
18. A. Bukowska, W. Bukowski, K. Bester, K. Hus, Polymer supported copper(II) amine-imine complexes in the C-N and A³ coupling reactions, *Appl Organomet. Chem.* **31** (2017).

<https://doi.org/10.1002/aoc.3847>

19. X. Ge, X. Chen, C. Qian, S. Zhou, Efficient Ullmann C–N coupling catalyzed by a recoverable oligose-supported copper complex. *RSC Advances*. **6**, 58898–58906 (2016).
<https://doi.org/10.1039/C6RA13536F>
20. M. Nasrollahzadeh, M. Sajjadi, M. Shokouhimehr, R.S. Varma, Recent developments in palladium (nano)catalysts supported on polymers for selective and sustainable oxidation processes. *Coord Chem Rev*. **397**, 54–75 (2019). <https://doi.org/10.1016/j.ccr.2019.06.010>
21. R. Shu, G. Zhang, J. Zhang, X. Wang, M. Wang, Y. Gan, J. Shi, J. He, Synthesis and high-performance microwave absorption of reduced graphene oxide/zinc ferrite hybrid nanocomposite. *Mater Lett*. **215**, 229–232 (2018). <https://doi.org/10.1016/j.matlet.2017.12.108>
22. G. Wang, Z. Ding, L. Meng, G. Yan, Z. Chen, J. Hu, Magnetically recoverable 2-(aminomethyl)phenols-modified nanoparticles as a catalyst for Knoevenagel condensation and carrier for palladium to catalytic Suzuki coupling reactions. *Appl. Organomet. Chem*. **34**, e5907 (2020).
<https://doi.org/10.1002/aoc.5907>
23. M.A. Ghasemzadeh, B.M.H. Abdollahi, M. Babaei, Fe₃O₄@SiO₂-NH₂ core-shell nanocomposite as an efficient and green catalyst for the multi-component synthesis of highly substituted chromeno[2,3-b] pyridines in aqueous ethanol media. *Green Chem. Lett. Rev*. **8**, 40 (2015).
<https://doi.org/10.1080/17518253.2015.1107139>
24. F. Pazoki, J.A. Mehraban, M. Shamsayei, B. Bakhshi, R. Esfandiarpour, M.K. Miraki, A. Heydari, Azamichael Addition of 5-Substituted Tetrazole Catalysed By a Novel Nanoparticle Solid Base Catalyst Involving a Layered Zinc Hydroxide Supported on a Ferrite Core. *ChemistrySelect*. **4**, 2568–2575 (2019). <https://doi.org/10.1002/slct.201804070>
25. Y. Zhang, Y.U. Lili, Y. Yang, N. Jia, A non enzymatic glucose sensor based on electrodepositing Cu/graphene nanocomposite film modified electrode. *Journal of Shanghai Normal University* **42**, 37–43 (2013). <https://doi.org/10.3969/J.ISSN.1000-5137.2013.01.007>
26. P.P. Cellier, J.-F. Spindler, M. Taillefer, H.-J. Cristau, Pd/C-catalyzed room-temperature hydrodehalogenation of aryl halides with hydrazine hydrochloride. *Tetrahedron Lett*. **44**, 7191–7195 (2003). [https://doi.org/10.1016/S0040-4039\(03\)01789-1](https://doi.org/10.1016/S0040-4039(03)01789-1)

Tables

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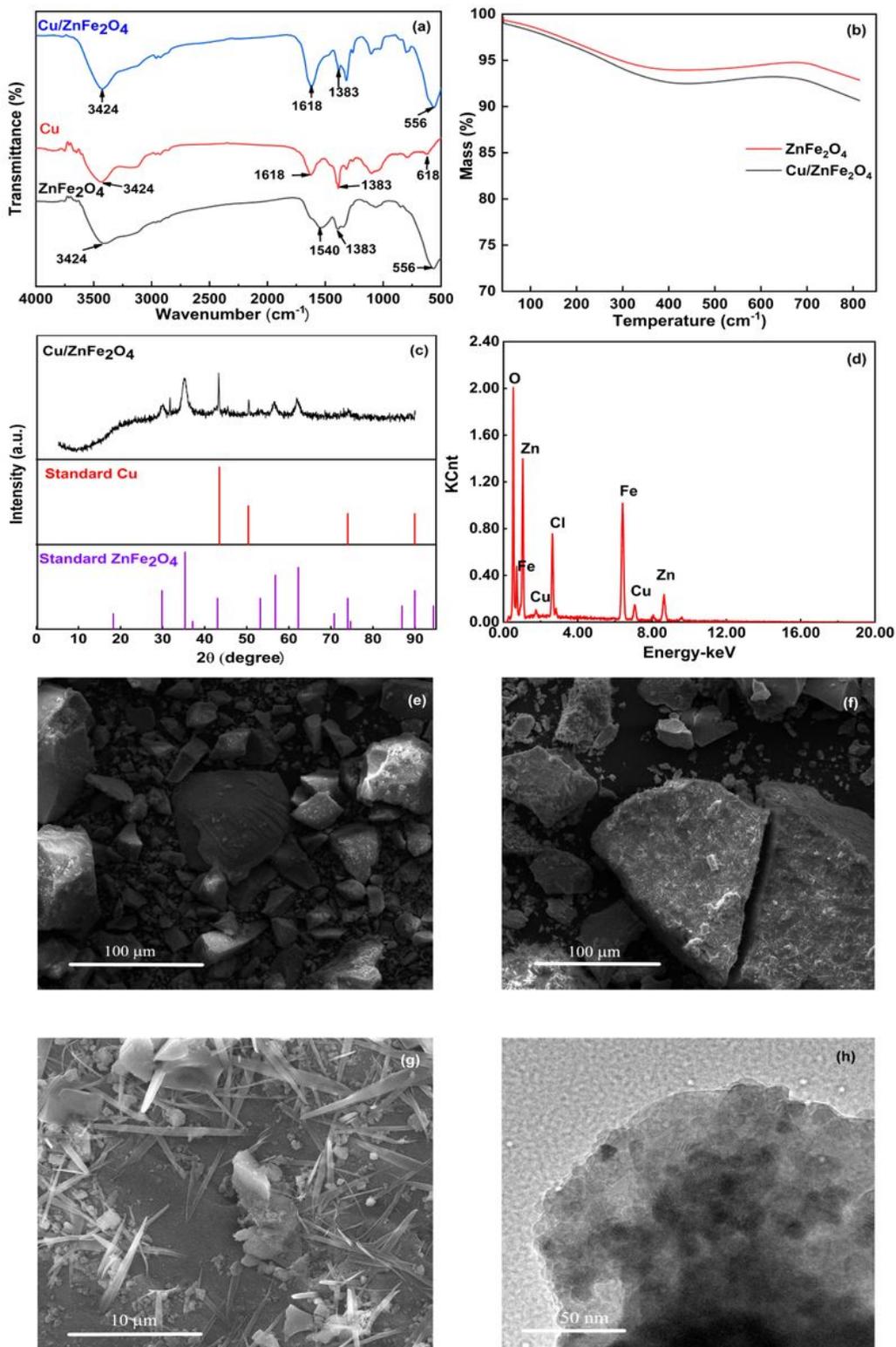


Figure 1

(a) FT-IR spectra of Cu/ZnFe₂O₄, Cu and ZnFe₂O₄; (b) TGA curves of Cu/ZnFe₂O₄ and ZnFe₂O₄; (c) XRD patterns of Cu/ZnFe₂O₄; (d) EDS image of Cu/ZnFe₂O₄; (e) SEM image of ZnFe₂O₄; (f) SEM image of Cu/ZnFe₂O₄; (g) SEM image of Cu/ZnFe₂O₄; (h) TEM image of Cu/ZnFe₂O₄.

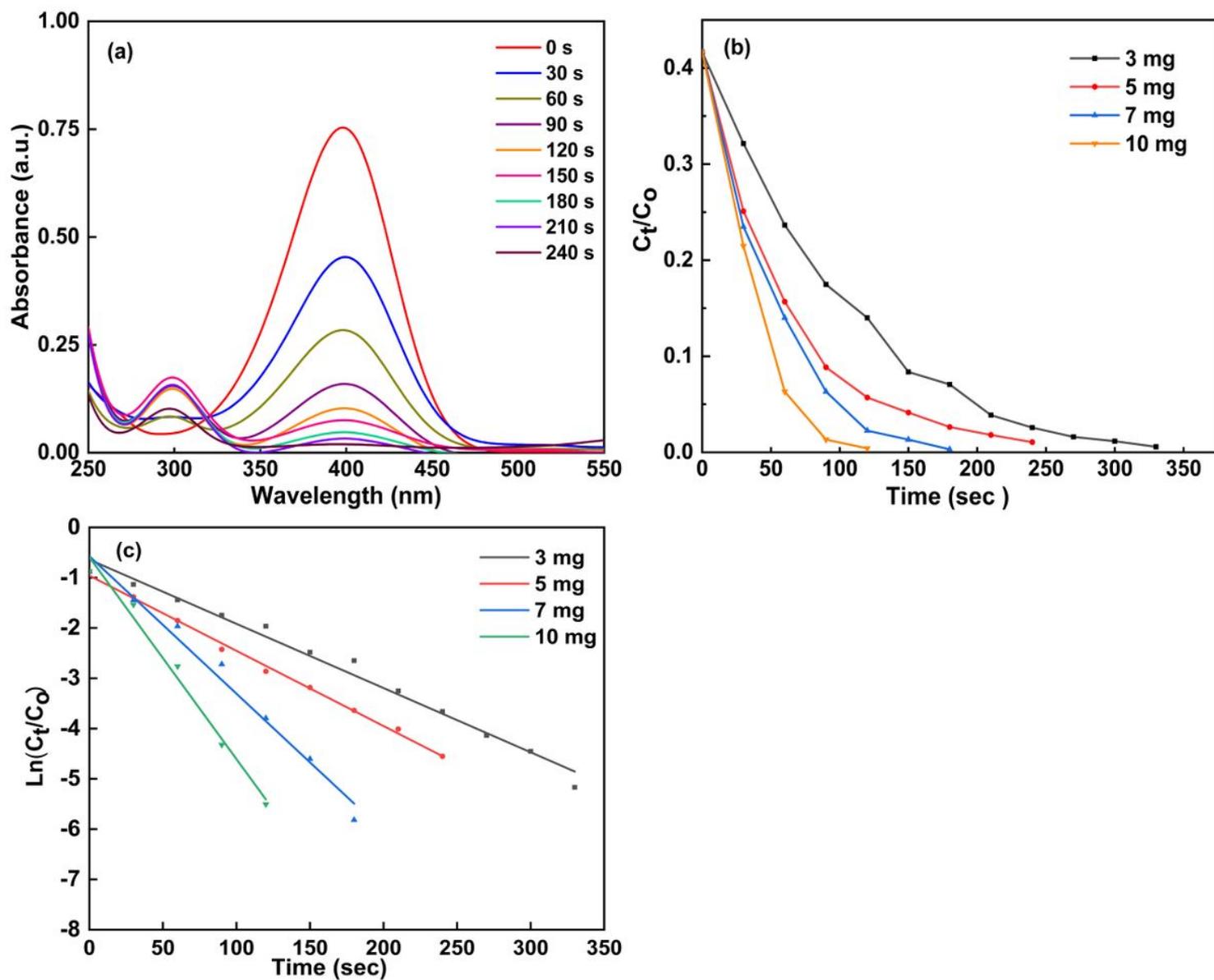


Figure 2

(a) UV spectra of and kinetic curves of the reduction of 4-NP to 4-AP. (b) influence of catalyst loading and reaction time on the reactivity. (c) kinetic curve of the reduction of 4-NP to 4-AP. (d) Catalytic reduction of other nitroarenes with Cu/ZnFe₂O₄ under optimized conditions.

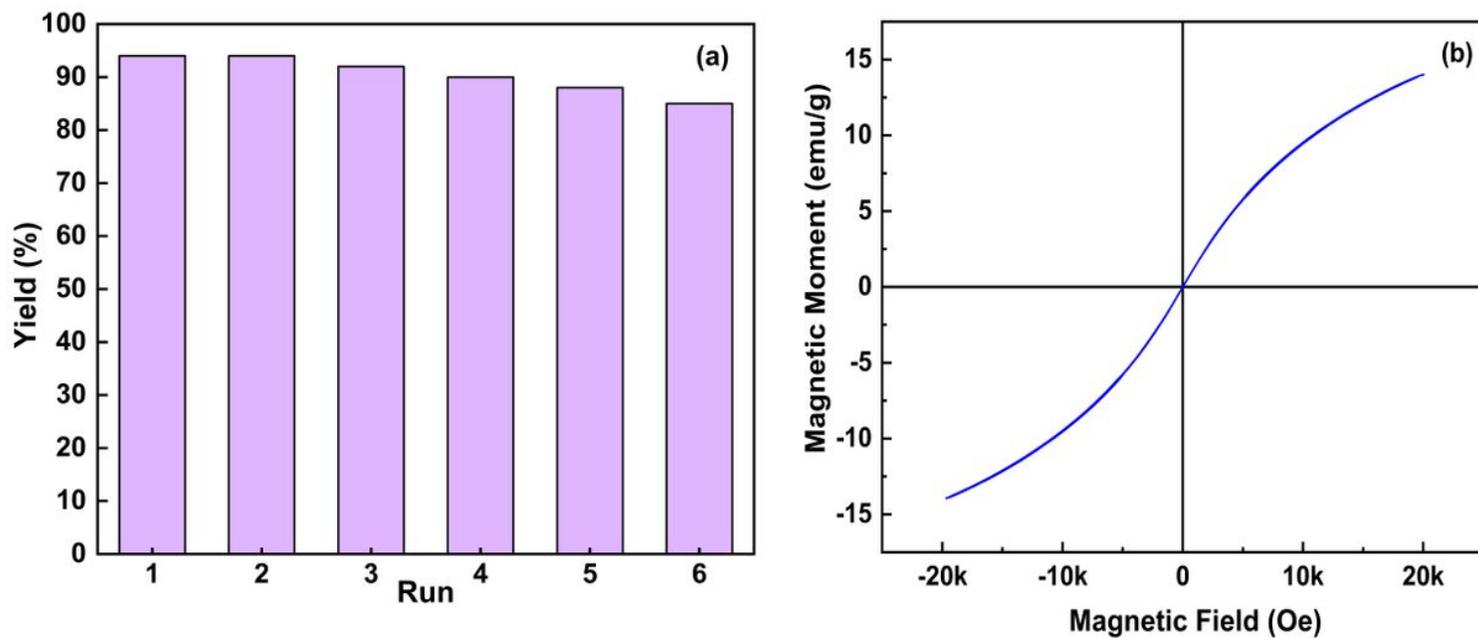


Figure 3

(a) Recyclability of the Cu/ZnFe₂O₄ catalyst. (b) VSM study of Cu/ZnFe₂O₄.

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