



MASTER DISSERTATION

Sustainable metal-organic framework derived-nanostructured catalysts for the heterogeneous reduction of nitroaromatics

By

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Sustainable metal-organic framework derived-nanostructured catalysts for the heterogeneous reduction of nitroaromatics

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Abstract

(MOF)-derived nanocatalysts Metal-organic framework various on nanostructured supports are generally efficient heterogeneous catalysts employable for organic transformations. Herein, nickel Prussian blue (PB) nanoparticles were deployed to form NiFe₂O₄ nanocatalysts supported on 2D molybdenum disulfide (MoS₂) through facile heat treatment. NiFe₂O₄ nanocatalysts could be uniformly dispersed on the high-specific-area MoS₂ surface, representing a highly efficient, inexpensive, and magnetically recoverable nanocomposite catalyst. The semiconductor property of MoS₂ ensures a high electric conductivity, thus enhancing electron transfer between the reductant and the reactant. Furthermore, the solid magnetic characteristics enable its convenient separation from the reaction mixture. NiFe2O4 nanoparticles on MoS₂-supported produces multiple electron transfer pathways and overcome known drawbacks of catalytic methods that use metals alone, endowing long-term cycle stability. Overall, MoS₂/NiFe₂O₄ exhibited excellent catalytic activity and high yields in the reduction of nitrobenzene in water, maintained even after five cycles.

Keywords: 2D material; Nitroaromatic reduction; metal-organic framework;

Magnetic catalyst; NiFe₂O₄

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Chapter 1

Catalytic transformations

1.1 Introduction

With the advent of resource scarcity, people focus on the rational utilization and development of advanced materials. Thus, as a result of environmental degradation, the catalytic technology based on green chemistry has attracted much attention. The word catalysis was first proposed by Berzelius in 1836¹. Catalysis is an important strategy affects human life, playing a central role in multidisciplinary research field including chemical. biological, nanotechnology, polymer, energy, pharmaceutical, and agriculture fields. In a catalytic reaction, the catalyst accelerates the reaction course by reducing the activation energy without affecting the thermodynamics of the overall reaction, thus altering the reaction process. Typically, a higher yield of the desired product can be obtained in a shorter time, while consuming less energy, than the corresponding stoichiometric reaction². In general, catalysts are classified into two categories, homogeneous and heterogeneous. In homogeneous catalysts, both reactants and catalysts are present in the same phase and active catalytic sites are easily accessible to reactants, resulting in enhanced catalytic activity and desirable product selectivity. It is also plausible to adjust the regio-,

chemo-, and enantio-selectivity of the reactions through appropriate selection of ligands, metals, and organocatalysts³. However, the recovery and recyclability of the heterogeneous catalysts is a major issue. Substantial production costs and time-consuming purification techniques are inevitable for the isolation of these catalysts from the reaction mixture. With the requirement of green chemistry, recovery and reuse of the catalysts are a vital issue for ecological and economical demands. Consequently, many methods have been explored for the development of heterogeneous catalysts with inherent capability of being easily isolated from the reaction mixture^{4,5}. Indeed, heterogeneous catalysts have the advantages of recovery and reuse after the completion of the reactions and green chemical processes⁶⁻⁸. Typically, immobilizing metal nanoparticles (NPs) on well-defined assorted solid supports is an indispensable method to assist their handling and separation⁹⁻¹¹. Heterogeneous catalysts are typically composed of two components: (i) support materials and (ii) active metal NPs¹². Most catalytically active heterogeneous catalysts intensely depend on precious metal NPs such as Pd, Ru, Rh, and Au. It should be noted that although the support materials can stabilize metal nanocatalysts and enhance their durability, they are generally

ineffective on the mechanism of catalytic processes^{13,14}. For instance, nonconducive supports have lack of electron motion even with exposure of high active sites or surface area. Properties of the catalyst support and the heterogenization process influence the performance of the heterogeneous nanocatalysts. The porous structure and pore size of the catalyst not only affect the molecular transport and diffusion, but also affect the mechanical properties and lifetime of the catalyst^{15,16}. Therefore, the development of highly active heterogeneous catalysts with good durability and stability is exceedingly demanding.

1.2. Reduction of Nitroaromatics

1.2.1 Catalytic hydrogenations

Catalytic hydrogenation was discovered at the end of last century. The selective catalytic hydrogenation is capable to selectively reduce a target functional group follow the demand. It is required when two or more functional groups coexist in a substrate, or there are different unsaturated substrates in the catalytic system, one of the functional groups (or substrates) preferentially undergo transformation, while the other functional groups remain intact. Common hydrogen donors are silane^{17,18}, alcohols¹⁹, carboxylic acids²⁰, hydrazine hydrate, and sodium borohydride^{21,22}. Reduction of nitroaromatics by nanocatalysts and sodium borohydride is undoubtedly one of the most useful and widely applicable methods owing to no complex highpressure device, low-cost, and facile to obtain hydrogen donor in catalytic hydrogenation, and has found numerous applications in organic synthesis in research laboratories and industrial processes. To date, catalytic hydrogenation has become a promising reduction strategy. During optimizing reaction conditions and preparation of efficient catalysts, many low-cost, highefficiency applications for selective reduction of various functional groups have been developed.

Generally, over 90 % chemical manufacturing relies on catalytic processes. The hydrogenation of nitroaromatic compounds to their amine counterparts is an important transformation in the organic synthesis^{23,24}. Aromatic amines are utilized in many industries, including agrochemicals, pharmaceuticals, polymers, dyes, and cosmetics, which produce a large variety of essential products^{25,26} (Figure 1).



Figure 1. Selected applications of functionalized aromatic amines in the production of agrochemicals, dyes, pharmaceuticals, and surfactants.

1.2.2 Reduction mechanism

The mechanism of the nitroaromatics hydrogenation was proposed by Haber²⁷. The transformation to aniline can be achieved in two different routes involving direct route and condensation route (Figure 2). First, the nitro group is reduced to nitroso group. Then, a second equivalent of hydrogen can result in the formation of corresponding hydroxylamine. Finally, the aniline is attained with the addition of a third equivalent hydrogen. In addition, azoxybenzene, azobenzene and hydrazobenzene can be formed as by-products via the reaction of two intermediate species.



Figure 2. The Haber mechanism for the hydrogenation of nitrobenzene to aniline.

These two reaction path can be identified by detecting the intermediates produced in the reduction of nitroaromatics. However, the intermediates are often difficult to be detected in the reaction solution. They are tightly adsorbed on the catalyst surface, and only can be detected and analyzed by *in situ* analysis and characterization methods. For instance, Avelino Corma *et al.* demonstrated the formation of nitrobenzene, phenylhydroxylamine and aniline on the surface of catalyst Au/TiO₂ using *in situ* infrared spectroscopy, excluding the presence of potential intermediates such as azobenzene, azobenzene oxide and hydrogenated azobenzene²⁸. Thus, it was illustrated that the transformation of -NO₂ into -NH₂ on Au/TiO₂ catalyst takes place through the direct transformation route.

In heterogeneous catalytic hydrogenation, the reduction mechanism is related with the catalyst and reducing agent and the interaction between catalyst with hydrogen donor and acceptor effect the transfer efficiency and pathway of hydrogen, which cause the different transformation process of reduction mechanism.

1.2.3 Heterogeneous catalysts for reduction of nitroaromatics

Catalytic hydrogenation performance can be attribute to developing highly efficient catalysts. Typically, catalysts as the active sites in hydrogen transfer process, which can be broadly divided into homogeneous catalysts and heterogeneous catalysts^{29,30}. Homogenous catalysts generally dissolve in reaction media, providing readily-accessible catalytic sites, resulting in mild reaction conditions and good selectivity³¹. However, they have limited applications due to the problems in separating the products and recycling 32,33 . In contrast, the active metal of heterogeneous catalyst is anchored on the solid support materials, showing appropriate potential for recovery, and reuse³⁴. Several methods have been developed to prepare durable and recyclable heterogeneous catalysts for the reduction of nitroaromatics. These catalysts are generally favorable from the sustainable point of view. For example, heterogeneous catalysts for reduction of nitroaromatics include noble metal NPs, e.g., Pt, Pd, Ru, Au, and non-noble metal NPs, e.g., Co, Ni, Cu. Precious metal nanocatalysts have high activity and good stability. Non-noble metals are expected to play an important role in the reduction of nitroaromatics instead of noble metal nanocatalysts because of their low cost and abundant reserves. However, their catalytic activity and cyclic stability is still challenging.

Due to the side reactions caused by excessive hydrogenation, the selectivity of nitroaromatics reduction expedited by heterogeneous catalysts is not still satisfactory^{35,36}. Many efforts have been realized that selectivity largely depends on the adsorption and configuration of the reactants/intermediates on the surface of the heterogeneous catalyst, which in turn depends on the electrons and geometry of the active sites³⁷. The size, composition, and shape of the active metal NPs in the heterogeneous catalysts can affect the catalytic selectivity^{38,39}. In particular, supported catalysts have a wide range of particle size distributions and may expose different crystal faces with different atomic structures. When focused on metal NPs, the metal atoms may be located at platforms, edges, corners, or metal-carrier interfaces, and each of these sites has a different coordination environment and electronic structure. These complex catalytic sites lead to different adsorption of reactants/intermediates, and therefore poor catalytic activity. Therefore, it is of great help for selective hydrogenation to design active catalysts reasonably and deepen the understanding of chemical reaction processes through theoretical calculation⁴⁰. In addition, exploring economical methods to prepare highly reactive, stable, scalable and recyclable heterogeneous catalysts remain as an important issue in the catalysis research field.

1.3 Metal-organic frameworks

Metal-organic frameworks (MOFs) have recently emerged as versatile materials in the field of heterogeneous catalysis⁴¹. It is a class of crystalline porous materials that contain strong coordination bonds between metal nodes and organic linkers to form extended structures. MOFs have emerged as a class of materials potentially capable of addressing catalytic challenges^{42,43}. The unique features of MOFs including high proportion of active sites, porosity, stability, reliable preparation procedures, and the possibility to synthesize them by design make them highly promising heterogeneous catalysts⁴⁴. For example, the high degree of synthetic adjustability available to MOFs allows for excellent control over relevant design properties, e.g., morphology, stability, porosity, and conductivity; the optimization of these parameters may potentially solve inherent drawbacks for the use of MOFs as highly appropriate heterogeneous catalysts. In particular, several organic transformations have been achieved by MOF-based catalysts⁴⁵.

The excellent catalytic activity and selectivity of MOFs-based catalysts facilitates various organic transformations in efficient and economical ways. MOFs-based catalysts enable sophisticated activity and selectivity regulation via catalytic engineering, such as ligand functionalization, metal node alternation, pore regulation, topology variation and so on. Consequently, MOFs-based materials have been widely recognized as appropriate catalysts for achieving exceptional size-, shape-, chemo-, regio-, and stereo-selectivity in various organic transformations. In addition, MOFs have been employed as precursors to form highly active nanocomposite catalysts based on their constitutive components.

1.4 Two-dimensional materials

The development of two-dimensional (2D) materials has attracted considerable attention in a wide range of research fields⁴⁶. These materials have similar atomic arrangements and chemical bond strengths in both dimensions and possess unique physical properties owing to the electron confinement and heat transfer in their platform⁴⁷. Following the discovery and isolation of graphene in 2004 by Geim and Novoselov, extensive studies on inorganic graphene analogs with weak van der Waals forces between layers have been reported. For example, transition-metal dichalcogenides (TMDs) are used as field-effect transistors and phototransistors, graphitic carbon nitride nanosheets (g-C₃N₄) are used as photocatalysts, and 2D MOFs are used for gas absorption⁴⁸. Owing to their unique physiochemical properties originating from their ultrathin thickness and morphology, 2D nanomaterials are applied in various applications, such as energy conversion/storage, catalysis, and electronics. To expand their application scope, 2D nanomaterials are coupled with metal NPs to form heterogeneous catalysts⁴⁹. In particular, due to their large surface-to-volume ratio and inert features, 2D nanomaterials have been used as supports for nanocatalysts to expedite organic

transformations⁵⁰. Nanocatalysts comprising immobilized metal NPs, such as Pd, Pt, Au, Ni, and Cu, on 2D nanomaterial supports can be adjusted for common organic reactions, such as the Suzuki–Miyaura, Heck, Ullmann, Sonogashira, and aromatics reduction reactions^{51,52}. However, metal-support catalysts often encounter critical deficiencies, including polydispersed particle size distribution, and different crystal planes with different atomic structures, which hinders their catalytic performance. For example, active metal atoms can exist on platforms, edges, kinks, steps, corners, terraces, and vacancies between the metal and support. These complex sites have different coordination structures, causing difficulties in catalytic activity and selectivity⁵³.

1.5 Magnetic nanostructured catalysts

With the emerging and deployment of green and sustainable chemistry, organic transformations embrace the restraint utilization of toxic reagents and organic solvents, expensive and unstable catalysts, and harsh reaction conditions. Recent applications of nanotechnology in the field of catalysis has provided the requirements of the highly active and stable catalysts. The incorporation of magnetic species in the nanostructured catalysts can substitute typical sophisticated separation and recycling of the heterogeneous catalysts such as filtration and centrifugation. Magnetic nanostructured catalysts can be simply separated from the reaction mixture applying external magnet and maintain their high catalytic activities because of complete recovery and avoidance of the agglomeration⁵⁴. Magnetic separation technique has been used for decades in catalytic processes to separate magnetic catalysts from products and reaction media. Numerous applications and opportunities have emerged for the advanced nanomaterial developments by combining magnetic properties. Magnetic NPs have garnered huge interests due to their characteristics and applications in catalysis⁵⁵. The heterogeneous catalysts containing magnetic NPs can easily be separated from the reaction mixture and reused in the next reaction. Magnetic separation resolves the necessity of laborious and impractical separation procedures for the recycling of the precious catalysts. It provides a practical method for the isolation and dispersion of the magnetized catalysts by applying and removing an appropriate magnetic field. This approach hampers the aggregation of the catalysts and improves their durability⁵⁶. To pursue the practical applications and developments of heterogeneous catalysts, hybrid magnetic nanocomposites have been designed and applied for various organic transformations, including reduction of nitroaromatics.

Reference

- Santoro, S., Ferlin, F., Luciani, L., Ackermann, L. & Vaccaro, L. Biomass-derived solvents as effective media for cross-coupling reactions and C-H functionalization processes. *Green Chem.* 19, 1601–1612 (2017).
- Lindström, B. & Pettersson, L. J. A Brief History of Catalysis.
 CATTECH 7, 130–138 (2003).
- Rothenberg, G. Catalysis: concepts and green applications. (John Wiley & Sons, 2017).
- 4. Choi, K. H., Shokouhimehr, M. & Sung, Y. E. Heterogeneous suzuki cross-coupling reaction catalyzed by magnetically recyclable nanocatalyst. *Bull. Korean Chem. Soc.* **34**, 1477–1480 (2013).
- Wang, Y., Li, H., Zhang, J., Yan, X. & Chen, Z. Fe₃O₄ and Au nanoparticles dispersed on the graphene support as a highly active catalyst toward the reduction of 4-nitrophenol. *Phys. Chem. Chem. Phys.* 18, 615–623 (2016).
- Shokouhimehr, M., Kim, J. H. & Lee, Y. S. Heterogeneous heck reaction catalyzed by recyclable polymer-supported N-heterocyclic

carbene-palladium complex. *Synlett* 618–620 (2006) doi:10.1055/s-2006-932467.

- Janssen, M., Müller, C. & Vogt, D. Recent advances in the recycling of homogeneous catalysts using membrane separation. *Green Chem.* 13, 2247–2257 (2011).
- Kim, J.-H., Kim, J.-W., Shokouhimehr, M. & Lee, Y.-S. Polymersupported N-heterocyclic carbene– palladium complex for heterogeneous Suzuki cross-coupling reaction. *J. Org. Chem.* 70, 6714–6720 (2005).
- Hong, K. *et al.* Palladium Nanoparticles on Assorted Nanostructured Supports: Applications for Suzuki, Heck, and Sonogashira Cross-Coupling Reactions. *ACS Appl. Nano Mater.* 3, 2070–2103 (2020).
- Fu, Q. *et al.* Boron nitride nanosheet-anchored pd-fe core-shell nanoparticles as highly efficient catalysts for suzuki-miyaura coupling reactions. *ACS Appl. Mater. Interfaces* 9, 2469–2476 (2017).
- Baran, T., Inanan, T. & Menteş, A. Synthesis, characterization, and catalytic activity in Suzuki coupling and catalase-like reactions of new chitosan supported Pd catalyst. *Carbohydr. Polym.* 145, 20–29 (2016).

- Hu, Z. N. *et al.* Insight into the selectivity of nano-catalytic nitroarenes reduction over other active groups by exploring hydrogen sources and metal components. *Applied Catalysis A: General* vol. 626 (2021).
- Polshettiwar, V., Len, C. & Fihri, A. Silica-supported palladium: Sustainable catalysts for cross-coupling reactions. *Coord. Chem. Rev.* 253, 2599–2626 (2009).
- Rafiaei, S. M., Kim, A. & Shokouhimehr, M. Gadolinium triflate immobilized on magnetic nanocomposites as recyclable Lewis acid catalyst for acetylation of phenols. *Nanosci. Nanotechnol. Lett.* 6, 309–313 (2014).
- Li, H., Zhu, Z., Liu, J., Xie, S. & Li, H. Hollow palladium–cobalt bimetallic nanospheres as an efficient and reusable catalyst for Sonogashira-type reactions. *J. Mater. Chem.* 20, 4366–4370 (2010).
- Zhao, D., Wan, Y. & Zhou, W. Ordered mesoporous materials. (John Wiley & Sons, 2012).
- Sorribes, I., Junge, K. & Beller, M. Direct catalytic N-alkylation of amines with carboxylic acids. J. Am. Chem. Soc. 136, 14314–14319

(2014).

- Fu, M., Shang, R., Cheng, W. & Fu, Y. Boron-catalyzed N-alkylation of amines using carboxylic acids. *Angew. Chemie Int. Ed.* 54, 9042– 9046 (2015).
- Jiang, L., Guo, H., Li, C., Zhou, P. & Zhang, Z. Selective cleavage of lignin and lignin model compounds without external hydrogen, catalyzed by heterogeneous nickel catalysts. *Chem. Sci.* 10, 4458– 4468 (2019).
- Andrews, K. G., Summers, D. M., Donnelly, L. J. & Denton, R. M. Catalytic reductive N-alkylation of amines using carboxylic acids. *Chem. Commun.* 52, 1855–1858 (2016).
- Trillo, P., Slagbrand, T. & Adolfsson, H. Straightforward α-Amino Nitrile Synthesis Through Mo (CO)₆-Catalyzed Reductive Functionalization of Carboxamides. *Angew. Chemie* 130, 12527– 12531 (2018).
- Shah, P. R., Vohs, J. M. & Gorte, R. J. Redox isotherms for vanadia supported on zirconia. *Catal. Letters* 125, 1–7 (2008).
- 23. Han, S. et al. Selective oxidation of anilines to azobenzenes and

azoxybenzenes by a molecular Mo oxide catalyst. *Angew. Chemie* **133**, 6452–6455 (2021).

- Zhao, J.-X. *et al.* Selectivity regulation in Au-catalyzed nitroaromatic hydrogenation by anchoring single-site metal oxide promoters. *ACS Catal.* 10, 2837–2844 (2020).
- 25. Zeynizadeh, B. & Gilanizadeh, M. Green and highly efficient approach for the reductive coupling of nitroarenes to azoxyarenes using the new mesoporous Fe₃O₄@ SiO₂@ Co–Zr–Sb catalyst. *Res. Chem. Intermed.* 46, 2969–2984 (2020).
- Liu, L., Concepción, P. & Corma, A. Modulating the catalytic behavior of non-noble metal nanoparticles by inter-particle interaction for chemoselective hydrogenation of nitroarenes into corresponding azoxy or azo compounds. *J. Catal.* 369, 312–323 (2019).
- Gelder, E. A., Jackson, S. D. & Lok, C. M. The hydrogenation of nitrobenzene to aniline: a new mechanism. *Chem. Commun.* 522–524 (2005).
- Corma, A., Gonzalez-Arellano, C., Iglesias, M. & Sánchez, F. Gold complexes as catalysts: Chemoselective hydrogenation of nitroarenes.

Appl. Catal. A Gen. 356, 99-102 (2009).

- Toebes, M. L., van Dillen, J. A. & de Jong, K. P. Synthesis of supported palladium catalysts. *J. Mol. Catal. A Chem.* 173, 75–98 (2001).
- Benaglia, M. & Puglisi, A. Catalyst immobilization: methods and applications. (John Wiley & Sons, 2019).
- Dijkstra, H. P., Van Klink, G. P. M. & Van Koten, G. The use of ultra-and nanofiltration techniques in homogeneous catalyst recycling. *Acc. Chem. Res.* 35, 798–810 (2002).
- Desset, S. L. & Cole-Hamilton, D. J. Carbon Dioxide Induced Phase Switching for Homogeneous-Catalyst Recycling. *Angew. Chemie* 121, 1500–1502 (2009).
- Copéret, C., Chabanas, M., Petroff Saint-Arroman, R. & Basset, J. Homogeneous and heterogeneous catalysis: bridging the gap through surface organometallic chemistry. *Angew. Chemie Int. Ed.* 42, 156– 181 (2003).
- 34. Van Santen, R. A. Modern heterogeneous catalysis: an introduction.(John Wiley & Sons, 2017).

- Studer, M., Neto, S. & Blaser, H.-U. Modulating the hydroxylamine accumulation in the hydrogenation of substituted nitroarenes using vanadium-promoted RNi catalysts. *Top. Catal.* 13, 205–212 (2000).
- Climent, M. J., Corma, A. & Iborra, S. Heterogeneous catalysts for the one-pot synthesis of chemicals and fine chemicals. *Chem. Rev.* 111, 1072–1133 (2011).
- Lear, T. *et al.* The application of infrared spectroscopy to probe the surface morphology of alumina-supported palladium catalysts. *J. Chem. Phys.* 123, 174706 (2005).
- Zhou, K. & Li, Y. Catalysis based on nanocrystals with well-defined facets. *Angew. Chemie Int. Ed.* 51, 602–613 (2012).
- Strasser, P. *et al.* Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts. *Nat. Chem.* 2, 454–460 (2010).
- Andersin, J. & Honkala, K. First principles investigations of Pd-on-Au nanostructures for trichloroethene catalytic removal from groundwater. *Phys. Chem. Chem. Phys.* 13, 1386–1394 (2011).
- 41. Furukawa, H., Cordova, K. E., O'Keeffe, M. & Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science*

(80-.). **341**, (2013).

- 42. Lee, J. *et al.* Metal-organic framework materials as catalysts. *Chem. Soc. Rev.* **38**, 1450–1459 (2009).
- Wei, Y.-S., Zhang, M., Zou, R. & Xu, Q. Metal–organic framework-based catalysts with single metal sites. *Chem. Rev.* 120, 12089–12174 (2020).
- Xu, C., Fang, R., Luque, R., Chen, L. & Li, Y. Functional metal– organic frameworks for catalytic applications. *Coord. Chem. Rev.* 388, 268–292 (2019).
- Yang, D. & Gates, B. C. Catalysis by metal organic frameworks: perspective and suggestions for future research. *Acs Catal.* 9, 1779– 1798 (2019).
- Frisenda, R. *et al.* Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials. *Chem. Soc. Rev.* 47, 53–68 (2018).
- Zhang, X. & Xie, Y. Recent advances in free-standing twodimensional crystals with atomic thickness: Design, assembly and transfer strategies. *Chem. Soc. Rev.* 42, 8187–8199 (2013).
- Zhang, J., Chen, Y. & Wang, X. Two-dimensional covalent carbon nitride nanosheets: Synthesis, functionalization, and applications. *Energy Environ. Sci.* 8, 3092–3108 (2015).
- 49. Huang, X. *et al.* Coating two-dimensional nanomaterials with metalorganic frameworks. *ACS Nano* **8**, 8695–8701 (2014).
- Scheuermann, G. M., Rumi, L., Steurer, P., Bannwarth, W. & Mülhaupt, R. Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the Suzuki-Miyaura coupling reaction. *J. Am. Chem. Soc.* 131, 8262–8270 (2009).
- Sharavath, V. & Ghosh, S. Palladium nanoparticles on noncovalently functionalized graphene-based heterogeneous catalyst for the Suzuki-Miyaura and Heck-Mizoroki reactions in water. *RSC Adv.* 4, 48322– 48330 (2014).
- Dreyer, D. R., Jia, H.-P. & Bielawski, C. W. Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions. *Angew. Chemie* 122, 6965–6968 (2010).
- 53. Yan, H. et al. Atomic engineering of high-density isolated Co atoms

on graphene with proximal-atom controlled reaction selectivity. *Nat. Commun.* **9**, (2018).

- Gawande, M. B., Branco, P. S. & Varma, R. S. Nano-magnetite (Fe₃O₄) as a support for recyclable catalysts in the development of sustainable methodologies. *Chem. Soc. Rev.* 42, 3371–3393 (2013).
- Polshettiwar, V. *et al.* Magnetically recoverable nanocatalysts. *Chem. Rev.* 111, 3036–3075 (2011).
- Baig, R. B. N. & Varma, R. S. Magnetically retrievable catalysts for organic synthesis. *Chem. Commun.* 49, 752–770 (2013).
- 57. Blaser, H. U. *et al.* Selective Hydrogenation for Fine Chemicals:
 Recent Trends and New Developments. *Adv. Synth. Catal.* 345, 103–151 (2003).

Chapter 2

MOF-derived NiFe₂O₄ nanoparticles on molybdenum disulfide: Magnetically reusable nanocatalyst for the reduction of nitroaromatics in aqueous media

2.1 Introduction

The hydrogenation of nitroaromatic compounds to their amine counterparts is an important means of organic synthesis and transformation. Functionalized aromatic amines are employed in many industries, such as agrochemicals, pharmaceuticals, polymers, dyes, and cosmetics, which produce a large variety of essential intermediates used in laboratories and industries^{57,58}. Typically, these chemical processes are achieved by catalytic transformations. In practice, heterogeneous catalysts are preferred over homogeneous ones owing to their low cost, reusability, and stability^{59,60}. However, critical drawbacks, such as low catalytic efficiency and sophisticated preparation, hinder their industrial applications. Immobilizing metal nanoparticles (NPs) on well-defined assorted solid supports is a fundamental method for resolving these issues. Heterogeneous catalysts are typically composed of two components: (i) support materials and (ii) active metal NPs. Most catalytically active heterogeneous catalysts strongly depend on precious metal NPs such as Pd, Ru, Rh, and Au⁶¹⁻⁶³. In addition, although the support materials can stabilize metal nanocatalysts and enhance the durability of the nanocatalysts, they are generally benign and ineffectual on the mechanism of catalytic processes. For

example, non-conducive supports suffer from lack of electron motion even with exposure of high active sites. Therefore, they do not affect the activity of nanocatalysts in the electron-mediated catalytic processes ⁶⁴⁻⁶⁶. Dong et al. reported that mesoporous silica nanospheres could be used as a support material for bimetallic Pd–Ni⁶⁷ where it exhibited a high catalytic activity as supported nanocatalysts than unsupported Pd–Ni NPs. Shokouhimehr et al. designed and synthesized a magnetically recyclable hollow nanocomposite Pd catalyst⁶⁸ which displayed a high catalytic activity owing to its unique morphology. Gawande et al. fabricated magnetically separable and recyclable gold nanocatalysts, and the afforded yields of products reflected a good catalytic efficiency⁶⁹.

Hence, solid supports, such as carbon^{70,71}, silica⁷², zeolite⁷³, and polymers⁶, often through an altered process to reassemble a porous structure that can easily be incorporated with active metal NPs, have been used to enhance the stability and catalytic activity. Despite these remarkably high efficiencies, the exquisite structures of the support materials require higher preparation costs and thoughtful design⁷⁴⁻⁷⁸. These complex procedures and the inevitable use of noble metals gradually have become the drawbacks associated with

catalytic systems. Hence, there is a need to explore alternative co-catalysts based on relatively abundant transition metals. In recent years, molybdenum disulfide (MoS₂) has garnered extensive attention owing to its graphene–like 2D structure as it exhibits a sandwich structure held together by van der Waals forces. Moreover, MoS₂ is an n-type semiconductor with an indirect band gap^{79} . Previous studies have shown that MoS_2 has a high catalytic efficiency owing to the high electron mobility⁸⁰. In view of such several advantages, we believe MoS₂ can overcome the drawbacks associated with a huge waste stream of metal salts by deploying it as a composite along with active metals. Owing to its semiconductor property, MoS₂ shows good electron conductivity, which facilitates the electron transfer to the reactant from the reducing agent, enabling a high catalytic efficiency. Therefore, we attempted to synthesize NiFe₂O₄, a ferrimagnetic oxide with an inverse spinel structure on $MoS_2^{81,82}$. Generally, NiFe₂O₄ with oxygen vacancies exhibits a high catalytic activity after attaching the $-NO_2$ bond⁸³.

Moreover, the NiFe₂O₄ composite with MoS₂ solves two problems: the high costs of noble metals and the complicated structures of support materials. In addition, NiFe₂O₄ is considered to exhibit ferrimagnetism, attributed to the

inverse spin magnetic moment between the Fe³⁺ and Ni²⁺ ions⁸⁴. Magnetic NPs have recently attracted much attention in a variety of fields^{85,86}. Their innate magnetic moments can be utilized to make the catalyst magnetic for easy separation from the reaction system with the help of an external magnetic field.

Herein, we synthesized Prussian blue analogs (PBAs) as precursors mixed with MoS₂. After a facile heat treatment, decomposition into NiFe₂O₄ NPs decorated on MoS₂ takes place, resulting in a low-cost, stable, reusable, and noble metal–free magnetically recyclable Ni nanocatalyst (MR–MoS₂–Ni).

2.2 Experimental and methods

Materials and characterizations

Molybdenum disulfide (MoS₂), potassium ferricyanide (III) (K₃[Fe(CN)₆]), and nickel nitrate (II) hexahydrate Ni(NO₃)₂ were used for the chemical synthesis; these were purchased from Sigma-Aldrich. The other chemicals used in this study were purchased from the Daejung and Samchun chemical companies. The MR-MoS₂-Ni nanocatalyst with a nanocomposite structure was characterized using X-ray diffraction (XRD, D8-Advance), Raman spectroscopy (LabRAM HV Evolution), Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50), and electron spin resonance spectroscopy (ESR, JEOL JES-FA200). In addition, the morphology of the nanocatalyst was examined using a transmission electron microscope (TEM), a high-resolution TEM (HRTEM) and selected area electron diffraction (SAED, JEOL JEM-2100F) instrument with an energy dispersive spectrometer (EDS), and a fieldemission scanning electron microscope (FESEM, Zeiss, SUPRA 55VP).

The surface area of the MR-MoS₂-Ni composite nanocatalyst was analyzed using a Brunauer-Emmett-Teller device (BET, Micromeritics 3Flex) with the Barrett-Joyner-Halenda (BJH) method to study the pore size. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian 730ES) was used to determine the concentrations of the various metal species. The chemical state of the nanocatalyst was identified using an X-Ray photoelectron spectroscope (XPS, AXIS-His) with the Al K α X-ray source. The magnetic property was investigated using a vibrating-sample magnetometer (VSM-7410). Finally, the results of the catalytic reactions were analyzed using a gas chromatography mass spectrometer (GC-MS) with Agilent technologies 7693 autosampler.

Preparation of MR-MoS₂-Ni nanocatalyst

The MR-MoS₂-Ni nanostructure catalyst was synthesized using a facile and green method. First, 1 g of MoS₂ was dispersed in 50 mL of deionized water and stirred at room temperature for 15 min. Ni(NO₃)₂ (500 mg) and K₃Fe(CN)₆ (500 mg) were then dissolved in deionized water; after an ultrasonic treatment for 15 min, this solution was directly added to the MoS₂ solution. Subsequently, the mixture was vigorously stirred for 12 h at room temperature. After stirring, the product was obtained by centrifugation and washed with distilled water. Finally, the product was dried in an oven and annealed at 900 °C for 4 h under Ar and H₂ mixture gas flow to produce the MoS₂ supported NiFe₂O₄ NPs

composite nanocatalyst. The overall process for the typical synthetic route for the nanocatalyst, MR-MoS₂-Ni, is illustrated (Figure 3).



Figure 3. Schematic procedure for the preparation of MR-MoS₂-Ni nanocatalyst.

Catalytic reduction

In a typical procedure, 20 mL of deionized water was used to dissolve 0.15 mmol NaBH₄, and 0.1 mmol nitroaromatics was prepared. Next, the MR–MoS2–Ni (0.3 mol% Ni) nanocatalyst was directly added to the above system and the ensuing mixture was kept for 2 h under an air atmosphere. After completion of the reaction, the MR–MoS₂–Ni composite nanocatalysts were separated using a small magnet. GC–MS was applied to measure the yield of the amino aromatic groups.

2.3 Results and discussion

We envisioned a MOF–derived PB as suitable precursor. Initially, $Ni(NO_3)_2 \cdot 6H_2O$ and $K_3Fe(CN)_6$ were dissolved in deionized water. Next, the resulting deposition, for which the co-precipitation method is used⁸⁷, was mixed with MoS₂ powder stirred for 12 h and then treated at 900 °C under an Ar and H₂ mixture gas for additional 4 h. After heating, PB-structure NiHCFe was converted into NiFe₂O₄ via physical absorption and was uniformly deposited on the MoS₂ surface.

TEM and SEM were employed to investigate the size and morphology of MR-MoS₂-Ni nanocatalyst, for which a sheet-like MoS₂ morphology was observed (Figures 4a and d). The co-precipitation method for the synthesized NiHCFe NPs resulted in particles decorated on the sheet-like MoS₂ morphology (Figure 4b). After the heat treatment, MR-MoS₂-Ni nanocatalyst could be obtained while some amounts of NPs embedded on the MoS₂ scaffold could be noticed (Figures 4c). The morphology and nanostructure of the MR-MoS₂-Ni nanocatalyst were additionally investigated by TEM, HRTEM, and SAED. (Figures 5a-f). TEM images and EDS map of the elements revealed the formation of MR-MoS₂-Ni and well-dispersed NiFe₂O₄ NPs decorated on the MoS₂ framework with an average size of ~ 50 nm (Figure 5g-k). The surface and composition of the MR-MoS₂-Ni nanocatalyst were also studied by FESEM and EDS elemental mapping, with results showing that NiFe₂O₄ NPs were located on the MoS₂ scaffold (Figure 6).

The nanosized structure of MR-MoS₂-Ni provides accessible pathways for the reagents to easily infiltrate the nanocatalyst. To analyze the composition of the metal inserted on MoS₂, X-ray diffraction was performed, which revealed peaks at (111), (331), (222), (400), (422), and (511) of NiFe₂O₄ NPs (Figure 7a). Furthermore, inductively coupled plasma (ICP) analysis of the MR–MoS₂–NiFe₂O₄ showed the existence of Ni element with ca. 0.3 mol%. The thermal stability investigation of MoS₂ and MR-MoS₂-Ni nanocomposite was conducted as presented in Figure 7b. The obtained data were analyzed by thermogravimetric analysis (TGA) under inert gas atmosphere at a temperature rate of ~10 °C/min. As illustrated, the MR-MoS₂-Ni curve comprise of essentially two parts. The first mass reduction in the temperature range of 30-100 °C indicates water and impurity decomposition. In comparison with MoS₂, MR-MoS₂-Ni nanocatalyst exhibits a higher porosity structure, leading to easy absorption of water. The second mass loss of MR-

MoS₂-Ni catalyst is ~8.5% more than that of MoS₂ as a whole. It mutually affirms the formation of MR-MoS₂-Ni nanocatalyst which is in consonance with the EDS elemental mapping of the components present in the prepared nanocatalyst.

To further analyze the structure of MR-MoS₂-Ni nanocatalyst, FT-IR was applied (Figure 7c). The characteristic bands at 614.69 cm^{-1} are attributed to Mo-S stretching vibration. Compared to pure MoS₂, the S-S vibration peak at 885 cm⁻¹ exhibited a redshift. Apart from the above characteristic peaks, the vibration of MR-MoS₂-Ni nanocatalyst is almost like pure MoS₂. Raman spectroscopy was performed to precisely analyze the MR-MoS₂-Ni nanocatalyst (Figure 7d) wherein the spectrum exhibited two symbolic peaks, namely A1g (the out-of-plane vibration of the S atoms) and E2g (the in-plane vibration of the Mo-S bonds), at 402 cm⁻¹ and 377 cm⁻¹, respectively. To investigate the specific surface area of MR-MoS₂-Ni nanocatalyst and MoS₂, nitrogen adsorption-desorption isotherms with BET pore size distribution were measured. These obtained curves of MR-MoS2-Ni nanocatalyst indicated that the surface area of the MR-MoS₂-Ni is 11.3819 m² g⁻¹ and the mainly related pore size of MR-MoS₂-Ni distributed ~3 nm (Figures 8a, b).

To confirm the surface chemical states of the nanocatalysts, XPS was performed. The survey spectrum shows that the dominant elements are C, O, S, Mo, Fe, and Ni (Figure 9a). The C 1s was assigned 284.8 eV, 288.55 eV and 292.62 eV, representing the peaks of C=C/C-C, C =O and C-O, (Figure 9b). The S element is divided into two peaks at 161.90 eV and 167.13 eV (Figure 9e). In addition, there is a peak of C–SO₂ bound to carbon at 293 eV (Figure 9e). The spectrum of the Mo element revealed two strong peaks of 232.15 eV and 228.80 eV, pointing to Mo $3d_{3/2}$ and Mo $3d_{5/2}$, respectively, and part of MoOx (Figure 9d). Then Ni 2p spectrum of MR-MoS₂-Ni, the main chemical states of Ni^{2+} are distributed at binding energies of 855.40 eV and 871.40 eV (Figure 9f). The Fe spectrum of MR-MoS₂-Ni was divided to 723 eV and 710 eV of binding energies (Figure 9g). Additionally, the transition metal (Fe, Ni)formed Ni-O-Fe linkage facilitating oxygen vacancies, promoting the conversion of the nitro group to the amino group. To clarify the O 1s XPS spectra, it was deconvoluted into three components: surface absorbed oxygen (~533 eV), oxidative oxygen (~531 eV), and lattice oxygen (~530 eV) (Figure 9c). The high oxidative oxygen species content (~53.2%) reflects the presence of surface oxygen vacancies in the nanocatalysts. The high oxygen ion

diffusion rate and electrical conductivity can be attributed to the oxygen vacancies. Furthermore, the ESR spectrum (Figure 10), with observed g = 2.00 signal, indicates electron trapped centers in MR-MoS₂-Ni nanocatalyst.



Figure 4. SEM images of (a) MoS₂, (b) MoS₂-NiHCFe, and (c) MR-MoS₂-Ni nanocatalyst. (d) TEM image of MoS₂.



Figure 5. (a-c) TEM, (d-f) HRTEM, and (g) STEM images of MR-MoS₂-Ni nanocatalyst. The inset of (e) shows the relevant SAED pattern. The inset of (f) shows the relevant interplanar spacing. EDS elemental mapping of (h) Fe, (i) Ni, (j) Mo, (k) S for MR-MoS₂-Ni nanocatalyst.



Figure 6. (a and b) FESEM images, (c) EDS spectrum, and (d-g) EDS elemental mapping of Mo, S, Ni, Fe of the as-prepared MR-MoS₂-Ni nanocatalyst. Zr peak is related to the sample holder. Pt peak is related to the Pt coating of the sample.



Figure 7. (a) XRD pattern of MR-MoS₂-Ni nanocatalyst. (b) TGA analyses of MoS₂ and MR-MoS₂-Ni nanocatalyst. (c) FT-IR spectra of MoS₂ and the MR-MoS₂-Ni nanocatalyst. (d) Raman spectra of MoS₂ and the MR-MoS₂-Ni nanocatalyst.



Figure 8. (a) Nitrogen adsorption-desorption isotherms and (b) the relevant pore volume and pore size of MoS_2 and MR-MoS₂-Ni nanocatalyst.



Figure 9. XPS spectra of (a) survey scan, (b) C 1s, (c) O 1s, (d) Mo 3d, (e) S 2p, (f) Ni 2p, (g) Fe 2p for MR-MoS₂-Ni nanocatalyst.



Figure 10. ESR spectrum of MR-MoS₂-Ni nanocatalyst.

Catalytic activity

The catalytic activity of MR-MoS₂-Ni nanocatalyst was evaluated in the reaction of 4-nitrobenzene to 4-aminobenzene by deploying aqueous NaBH₄. A high yield of 99% was obtained for the model reaction of nitrobenzene reduction (Table 1, entry 1). To further explore the reduction range and limitation of aromatic nitro compounds, various nitro substrates, such as –Cl, –Br, –CH₃, –NH₃, and –NHCOCH₃, were selected as reactants and investigated under environmentally safe conditions. The MR-MoS₂-Ni nanocatalyst showed high yields for all the nitroaromatic compounds that were reduced to their corresponding amino aromatic compounds. Furthermore, when two reducible groups coexisted, only the nitro functional groups in the nitroaromatics were converted without any change in the other functional groups (Table 1, entries 2-8).

To investigate the correlation between MR-MoS₂-Ni and reaction activity, the hydrogenation process was studied by controlling the nanostructure of different catalysts for the reduction of nitrobenzene as model reaction under identical reaction condition. Firstly, only NiHCFe NPs was employed as catalyst (Table 2, entry 3). Figure 11 depicts FESEM images and EDS analysis of NiHCFe NPs. The reaction afforded a low yield ($\sim 3\%$) of aniline under identical conditions using NiHCFe NPs as catalyst; this result was the same as that obtained when no catalyst was used (Table 2, entry 2). However, with MoS₂ as a support of NiHCFe NPs, the catalytic efficiency could be improved to 66% (Table 2, entry 5). This is attributed to the MOF-derived PB structure, which provides the required porosity ensuring optimum contact between substrate and the catalyst; moreover, MoS₂ provides anchoring sites for NPs, preventing aggregation.

Interestingly, a satisfactory yield ($\sim 41\%$) could still be obtained when MoS2 itself was used as a catalyst (Table 2, entry 4). This result further demonstrates that the semiconductor properties of MoS₂ help ensure a good catalytic activity. However, only providing channels for the electron flow of reactants cannot effectively promote a maximum activity for the catalyst. NiHCFe was subsequently converted into NiFe₂O₄ as nanocatalyst for the hydrogenation of nitrobenzene, which exhibited an excellent performance ($\sim 99\%$ yield). Electrons flow through metals more easily and NiFe₂O₄ provides more oxygen vacancies that attract the nitro functional groups in nitroaromatics, enabling reactions to occur more quickly. MoS₂, as a functional support, is combined with nonprecious metals as a catalyst in the reaction and plays a synergistic role with the active metal. However, carbon or other substances have been used as catalysts in previous reports, which can only function as a carrier but cannot provide any reaction activity.

Moreover, it shows the existence of multiple electron transfer pathways in MR–MoS₂–Ni (Figure 12). The number of electron transfer pathways increases as Ni NPs are attached onto the MoS₂ structure, compared with the initial MoS₂ pathway (NaBH₄ to MoS₂ to nitroaromatics pathway, Figure 12a). Now, at least four pathways emerge: (i) NaBH₄ to NiFe₂O₄ to MoS₂ to nitroaromatics, (ii) NaBH₄ to MoS₂ to nitroaromatics, (iii) NaBH₄ to NiFe₂O₄ to NiFe₂O₄ to nitroaromatics, (iv) NaBH₄ to MoS₂ to NiFe₂O₄ to nitroaromatics (Figure 12b). Thus, a variety of routes coexist, resulting in the highest reaction efficiency of the catalyst.

To further demonstrate electron transfer pathways of MR-MoS₂-Ni nanocatalyst, we studied the charge density differences (CDD) of MR-MoS₂-Ni nanocatalyst and MoS₂. CDD analysis visualizes the charge redistribution of chemical bond or interactions by differences between charge densities of the case system of interest and the references. The Vienna atomic software

package (VASP) was utilized to calculate the charge density of various systems. NiFe₂O₄/MoS₂ was one-unit cell layer of Ni-top-terminated NiFe₂O₄ (111) slab located above the 1 monolayer of MoS₂, which was constructed from supercells to minimize the lattice mismatch below 5%. BH₄ from NaBH₄ was then located at the adjacent top of the topmost Ni atom of NiFe₂O₄/MoS₂ as an adsorbed system, BH₄ @NiFe₂O₄/MoS₂. Furthermore, a model study without NiFe₂O₄ NPS, that is BH₄ @MoS₂, was considered to compare and emphasize the role of NiFe₂O₄ NPS. The charge density differences invoked by introducing BH₄⁻ anion for BH₄⁻@NiFe₂O₄/MoS₂ and BH₄⁻@MoS₂ are visualized in Figures 13a, 13b, respectively. The isosurface criteria is 0.015 $e/bohr^3$. The yellow region stands for net positive charges while the cyan region shows the net negative charges. Net negative charges demonstrate the existence of excessive electrons that can be transferred to the surface of Ni (Figure 13a). By changing the isosurface criteria of visualizing CDD from $0.015 \ e/bohr^3$ to $0.05 \ e/bohr^3$, apparently BH₄⁻ induces the existence of excessive electron density on the adjacent Ni atom at the surface of BH₄⁻ @NiFe₂O₄/MoS₂ compared to BH₄ @MoS₂ (Figures 14a, b). The 2dimensional planar intersection also revealed that the presence of NiFe₂O₄

NPs leads to the excessive electron density on the substrate and the hydrogen atom site of the BH₄⁻ (Figures 13c, d), which are both beneficial for the reduction of nitro groups to the corresponding amines. In addition, the positive charge region was the antibonding state between BH₄⁻ and NiFe₂O₄/MoS₂ (Figure 13c), which means that BH₄⁻ anion was not adsorbed on NiFe₂O₄/MoS₂ but functioned as a reducing agent to provide additional electron density on the catalytic active site. Therefore, the predominance of NiFe₂O₄/MoS₂ over MoS₂ in reducing nitro group to amine with the help of BH₄⁻ anion was predicted from the computational calculation which is in consonance with the aforementioned experimental results.

Additionally, the good reusability and durability of the catalyst can bring significant economic benefits for the industrial application. Herein, NiFe₂O₄ NPs exhibit a strong magnetic property as affirmed by the magnetic saturation value through the VSM analysis. A strong hysteresis loop curve was observed (Figure 15a). This result shows that the MR-MoS₂-Ni nanocatalysts have strong magnetic properties thus enabling its easy separation (Figure 16). The reduction of nitrobenzene as a model reaction was examined for the recycling and reuse studies, and MR-MoS₂-Ni nanocatalyst could be recycled for five

consecutive cycles and still maintained a catalytic activity of over 85% (Figure 15b). The recycled MR-MoS₂-Ni nanocatalyst was investigated by FESEM and EDS elemental analyses confirming the persistent structure stability and elements distribution after recycling (Figure 17). Consequently, the leaching of Ni and Fe elements could be the reason for the catalytic decay, which was supported by ICP-AES analyses; Mo, Fe, and Ni species were detected (Table 3).

Entry	Nitroaromatics	Product	Yield (%) ^a
1	NO ₂	NH ₂	99
2	H ₂ N NO ₂	H ₂ N NH ₂	97
3	NO ₂ NH ₂	NH2 NH2	99
4	Br NO ₂	Br NH ₂	99 ^b
5	Cl NO ₂	CI NH2	93 ^b
6	NO ₂	NH ₂	98
7	NO ₂	NH ₂	99 ^ь
8	NO ₂	NH ₂	97
H_3C	COCHN [°] V	H ₃ COCHN ✓	

Table 1. Reduction of various nitroaromatic compounds using MR-MoS₂-Ni

 nanocatalyst in aqueous solution.



^aReaction conditions: Nitrobenzene (0.1 mmol), NaBH₄ (0.15 mmol), MR-MoS₂-Ni nanocatalyst (0.3 mol%), H₂O (20 mL), room temperature, and 2 h. GC-MS yield. ^bEthanol/water was used as the solvent.

Entry	Catalyst (0.3 mol%)	Yield (%)
1	MR-MoS ₂ -Ni	99
2	-	3
3	NiHCFe	3
4	MoS_2	41
5	MoS ₂ -NiHCFe	66
6	MoS ₂ .Fe	58

Table 2. Control studies for the catalytic performance of differentnanostructured catalysts for the reduction of nitrobenzene in 2 h.



Figure 11. (a-b) FESEM images of NiHCFe NPs. (c) EDS spectrum, and (d and e) EDS elemental mapping of Ni and Fe of the NiHCFe NPs. Zr peak is related to the sample holder. Pt peak is related to the Pt coating of the sample.



Figure 12. The proposed electron pathway for (a) MoS_2 and (b) MR-MoS₂-Ni nanocatalyst with multiple pathways.



Figure 13. Visualized CDD of (a) BH_4^- @NiFe₂O₄/MoS₂ and (b) BH_4^- @MoS₂ with the (c, d) isosurface criteria of 0.015 *e/bohr*³.


Figure 14. Visualized charge density differences of (a) $BH_4^-@NiFe_2O_4/MoS_2$ and (b) $BH_4^-@MoS_2$.



Figure 15. (a) VSM analysis of MR-MoS₂-Ni nanocatalyst. (b) Recycling test for the reduction of nitrobenzene to aniline by MR-MoS₂-Ni nanocatalyst.



Figure 16. Digital camera images of (a) before magnetic separation and (b) after magnetic separation for MR-MoS₂-Ni nanocatalyst in aqueous media.



Figure 17. (a and b) FESEM images, (c) EDS spectrum, and (d-g) EDS elemental mapping of Mo, S, Ni, Fe of the recycled MR-MoS₂-Ni nanocatalyst. Zr peak is related to the sample holder. Pt peak is related to the Pt coating of the sample.

Element	As-prepared MR-MoS ₂ -Ni	5th cycled MR-MoS ₂ -Ni (µg/L)
	(µg/L)	
Мо	2238702.000	2158696.000
Fe	296147.000	234924.000
Ni	369192.000	333406.000

Table 3. ICP analyses for the as-prepared MR-MoS₂-Ni nanocatalyst and thereused MR-MoS₂-Ni nanocatalyst after 5^{th} cycle.

Conclusions

A magnetically recoverable MoS₂ supported NiFe₂O₄ NPs-decorated nanocatalyst was designed as catalytically active material for the reduction of nitrocompounds. This nanocomposite is doped with iron so that the entire system is magnetic, which can facilitate the task of magnetic separation; ease of recycling is shown for five cycles, while maintaining more than 85% of the catalytic activity. To further improve the yield and avoid the use of precious metals, we tried to incorporate the Ni and Fe oxides into the MoS₂ nanosheets in an environmentally friendly, simple, and convenient manner, which helped effectively increase the electron transfer pathways in the process of nitrobenzene reduction. The characterization results obtained using XRD, Raman, FT-IR, BET, ESR, VSM, XPS, FESEM and TEM could validate that the composite has magnetic properties and can be successfully loaded onto MoS₂ nanosheets; higher yields (93–99%) were obtained for the reduction of nitroaromatic compounds to the corresponding amines.

Reference

- Westerhaus, F. A. *et al.* Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes. *Nat. Chem.* 5, 537–543 (2013).
- Shil, A. K. & Das, P. Solid supported platinum(0) nanoparticles catalyzed chemo-selective reduction of nitroarenes to Narylhydroxylamines. *Green Chem.* 15, 3421–3428 (2013).
- Schabel, T., Belger, C. & Plietker, B. A mild chemoselective Rucatalyzed reduction of alkynes, ketones, and nitro compounds. *Org. Lett.* 15, 2858–2861 (2013).
- Zhang, J. *et al.* Differences in the selective reduction mechanism of 4nitroacetophenone catalysed by rutile- And anatase-supported ruthenium catalysts. *Catal. Sci. Technol.* 10, 1518–1528 (2020).
- Lyu, J. *et al.* Size-dependent halogenated nitrobenzene hydrogenation selectivity of Pd nanoparticles. *J. Phys. Chem. C* 118, 2594–2601 (2014).
- 63. Li, K. *et al.* Carbon Deposition on Heterogeneous Pt CatalystsPromotes the Selective Hydrogenation of Halogenated Nitroaromatics.

ACS Appl. Mater. Interfaces (2021) doi:10.1021/acsami.1c11548.

- Shokouhimehr, M. Magnetically separable and sustainable nanostructured catalysts for heterogeneous reduction of nitroaromatics. *Catalysts* 5, 534–560 (2015).
- Ansari, A., Badhe, R. A. & Garje, S. S. Preparation of CdS-TiO₂Based Palladium Heterogeneous Nanocatalyst by Solvothermal Route and Its Catalytic Activity for Reduction of Nitroaromatic Compounds.
 ACS Omega 4, 14937–14946 (2019).
- 66. Malik, A. & Nath, M. Synthesis of Ag/ZIF-7 by immobilization of Ag nanoparticles onto ZIF-7 microcrystals: A heterogeneous catalyst for the reduction of nitroaromatic compounds and organic dyes. J. Environ. Chem. Eng. 8, 104547 (2020).
- 67. Dong, Z. *et al.* Ni@Pd core-shell nanoparticles modified fibrous silica nanospheres as highly efficient and recoverable catalyst for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol. *Appl. Catal. B Environ.* 162, 372–380 (2015).
- 68. Lee, J. E., Han, S. I. & Hyeon, T. Magnetically recyclable hollow nanocomposite catalysts for heterogeneous reduction of nitroarenes

and Suzuki reactions. Chem. Commun. 49, 4779-4781 (2013).

- 69. Gawande, M. B. *et al.* Magnetic gold nanocatalyst (nanocat-Fe-Au):
 Catalytic applications for the oxidative esterification and hydrogen transfer reactions. *Green Chem.* 16, 4137–4143 (2014).
- Zhang, K. *et al.* Facile synthesis of monodispersed Pd nanocatalysts decorated on graphene oxide for reduction of nitroaromatics in aqueous solution. *Res. Chem. Intermed.* 45, 599–611 (2019).
- Salahshournia, H. & Ghiaci, M. Pd-Pt/modified GO as an efficient and selective heterogeneous catalyst for the reduction of nitroaromatic compounds to amino aromatic compounds by the hydrogen source.
 Appl. Organomet. Chem. 33, 1–13 (2019).
- Narkhede, N., Uttam, B. & Rao, C. P. Calixarene-Assisted Pd Nanoparticles in Organic Transformations: Synthesis, Characterization, and Catalytic Applications in Water for C-C Coupling and for the Reduction of Nitroaromatics and Organic Dyes. *ACS Omega* 4, 4908–4917 (2019).
- 73. Sun, Q. *et al.* Zeolite-Encaged Single-Atom Rhodium Catalysts:Highly-Efficient Hydrogen Generation and Shape-Selective Tandem

Hydrogenation of Nitroarenes. *Angew. Chemie - Int. Ed.* **58**, 18570–18576 (2019).

- 74. Liu, J., Li, J., Jian, P. & Jian, R. Intriguing hierarchical Co@NC microflowers in situ assembled by nanoneedles: Towards enhanced reduction of nitroaromatic compounds via interfacial synergistic catalysis. *J. Hazard. Mater.* **403**, 123987 (2021).
- 75. Niakan, M. & Asadi, Z. Selective Reduction of Nitroarenes Catalyzed by Sustainable and Reusable DNA-supported Nickel Nanoparticles in Water at Room Temperature. *Catal. Letters* (2019) doi:10.1007/s10562-019-02741-7.
- Evangelista, V. *et al.* Highly active Au-CeO₂@ZrO₂ yolk-shell nanoreactors for the reduction of 4-nitrophenol to 4-aminophenol. *Appl. Catal. B Environ.* 166–167, 518–528 (2015).
- 77. Begildayeva, T. *et al.* Production of copper nanoparticles exhibiting various morphologies via pulsed laser ablation in different solvents and their catalytic activity for reduction of toxic nitroaromatic compounds. *J. Hazard. Mater.* **409**, 124412 (2021).
- 78. Pratibha & Rajput, J. K. Autocombustion-Promoted Synthesis of

Lanthanum Iron Oxide: Application as Heterogeneous Catalyst for Synthesis of Piperidines, Substituted Amines and Light-Assisted Degradations. *ChemistrySelect* **5**, 10863–10881 (2020).

- Li, X. & Zhu, H. Two-dimensional MoS₂: Properties, preparation, and applications. *J. Mater.* 1, 33–44 (2015).
- Wu, M. hong *et al.* Molybdenum disulfide (MoS₂) as a co-catalyst for photocatalytic degradation of organic contaminants: A review.
 Process Saf. Environ. Prot. 118, 40–58 (2018).
- Sivakumar, P., Ramesh, R., Ramanand, A., Ponnusamy, S. & Muthamizhchelvan, C. Synthesis and characterization of NiFe₂O₄ nanoparticles and nanorods. *J. Alloys Compd.* 563, 6–11 (2013).
- Iraqui, S., Kashyap, S. S. & Rashid, M. H. NiFe₂O₄ nanoparticles: An efficient and reusable catalyst for the selective oxidation of benzyl alcohol to benzaldehyde under mild conditions. *Nanoscale Adv.* 2, 5790–5802 (2020).
- Zemski, K. A., Justes, D. R. & Castleman, A. W. Studies of metal oxide clusters: Elucidating reactive sites responsible for the activity of transition metal oxide catalysts. *J. Phys. Chem. B* 106, 6136–6148

(2002).

- 84. Oladipo, A. A., Ifebajo, A. O. & Gazi, M. Magnetic LDH-based
 CoO–NiFe₂O₄ catalyst with enhanced performance and recyclability
 for efficient decolorization of azo dye via Fenton-like reactions. *Appl. Catal. B Environ.* 243, 243–252 (2019).
- Bakhtiarzadeh, Z. *et al.* Hydrothermal self sacrificing growth of polymorphous MnO₂ on magnetic porous carbon
 (Fe₃O₄@Cg/MnO₂): A sustainable nanostructured catalyst for activation of molecular oxygen. *Mol. Catal.* **509**, 111603 (2021).
- Gholipour, B. *et al.* Metal-free nanostructured catalysts: Sustainable driving forces for organic transformations. *Green Chem.* 23, 6223–6272 (2021).
- 87. Zakaria, M. B. & Chikyow, T. Recent advances in Prussian blue and Prussian blue analogues: synthesis and thermal treatments. *Coord. Chem. Rev.* 352, 328–345 (2017).

- Jinghan Wang¹, Jaehyun Kim¹, Jiwon Bo¹, Dokyoon Kim², Soo Young Kim³, Ki Tae Nam¹, Rajender S. Varma⁴, Ho Won Jang^{1,*}, Rafael Luque^{5,6*}, Mohammadreza Shokouhimehr^{1,*}, MOF-derived NiFe2O4 nanoparticles on molybdenum disulfide: Magnetically reusable nanocatalyst for the reduction of nitroaromatics in aqueous media, J. Ind. Eng. Chem 107,428-435.
- Jinghan Wang,^{1,+} Kent O Kirlikovali,^{2,+} Soo Young Kim,³ Dong-wan Kim,⁴ Rajender S. Varma,⁵ Ho Won Jang,^{1,*} Omar K. Farha,^{2,*} Mohammadreza Shokouhimehr^{1,*}, Metal organic framework-based nanostructure materials: applications for non-lithium ion battery electrodes, CrystEngComm 24, 2925-2947
- Jinghan Wang,[†] Sol A Lee,[†] Ho Won Jang,^{*} Mohammadreza Shokouhimehr^{*}, Emerging two-dimensional-based nanostructured catalysts for sustainable organic transformations, Langmuir. (Accepted).

 Kaiqiang Zhang, Jaehyun Kim, Kent O Kirlikovali, Jinghan Wang, Tae Hyung Lee, Soo Young Kim, Rajender S. Varma, Ho Won Jang,* Omar K. Farha,* Mohammadreza Shokouhimehr*, Magnetically recyclable nanocomposites via lanthanide-based MOFs grown on natural sea sponge: Screening hydrogenation of nitrophenol to aminophenol. Molecular Catalysis 528,112459.

다양한 나노 구조 지지체 상의 금속유기구조체 (MOF) 유래 나노 촉매는 일반적으로 유기물 반능에 사용할 수 있는 효율적인 이종 촉매이다. 여기에서는 니켈 프로이센 블루(PB) 나노입자를 배치하여 2D몰리브덴디설파이드(MoS₂)에 담지된 NiFe₂O₄ 나노촉매를 열처리를 통해 형성하였다. NiFe₂O₄ 나노 촉매는 고비면적 MoS₂ 표면에 균일하게 분산될 수 있으며, 이는 매우 효율적이고 저렴하며 자기적으로 회수 가능한 나노복합 촉매를 나타낸다. MoS, 의 반도체 특성은 높은 전기 전도도를 보장하여 환원제와 반응물 간의 전자 전달을 향상시킨다. 또한, 강한 자성 특성은 반응 혼합물로부터 쉽게 분리할 수 있다. MoS₂ 담지된 상의 NiFe₂O₄ 나노입자는 다수의 전자전달경로를 생성하고 금속만을 사용하는 촉매방법의 알려진 단점을 극복하여 장기적인 사이클 안정성을 제공한다. 전체적으로 MoS₂/NiFe₂O₄ 는

우수한 촉매 활성과 5 사이클 이후에도 유지되는 물 속 니트로벤젠의 환원 수율이 높은 것을 확인할 수 있었다. **주요어:** 이차원 재료, 니트로기 방향족 환원, 금속유기구조체, 자성 촉매, NiFe₂O₄.

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