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Magnetic metal-organic frameworks (MMOFs): As multipurpose catalysts

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Spotlight

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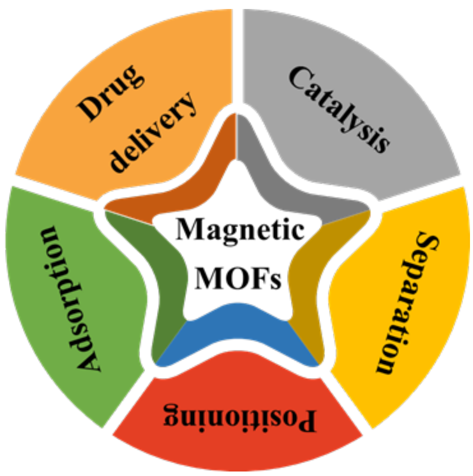
Milad Mohammadi Rasooll was born in Hamedan, Iran in 1995. He received his B.Sc. in pure Chemistry (2018) from Bu-Ali Sina University, Iran. He received his M.Sc. in Organic Chemistry (2021) under the supervision of Prof. Mohammad Ali Zolfigol. He was also accepted into a Ph.D. program in organic chemistry at the Bu-Ali Sina University in the same year. His research interests are the synthesis, characterization, and application of homogeneous and heterogeneous reagents and catalysts in organic synthesis.

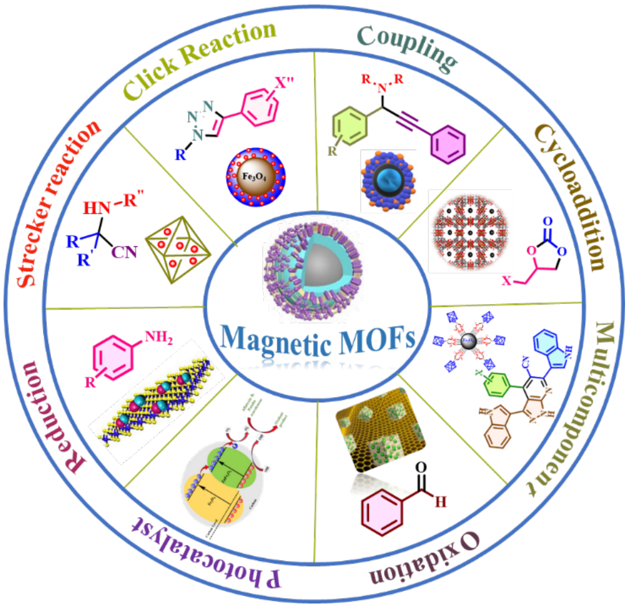
1. Introduction

Recently, material engineering chemistry has been studied, including the chemistry of materials with high porosity and surface area with many rich sites for chemical interactions [1, 2]. Metal-organic frameworks (MOFs), which are formed by connecting metal clusters to organic ligands and form a very regular 3D crystal network, are an attractive superclass of this category [3, 4]. The wide applications of MOFs, such as chemical sensors, drug delivery, energy storage, absorption of chemical pollutants, etc., have caused a lot of attention to be paid to this category of porous compounds in the last decade [5, 6]. In addition to the mentioned features, MOFs have high design capabilities, which makes them special and unique [7]. In recent years, increasing the stability of MOFs has been of great interest. An attractive perspective for this is the integration of MOFs with metallic nanoparticles (NPs) [8]. Magnetic iron nanoparticles (Fe_3O_4) are an amazing class of metallic nanoparticles, and for that reason, they have a high fraction of active atoms and a high surface-to-volume ratio [9]. Due to these characteristics, the integration of Fe_3O_4 and MOFs has been able to create compounds with interesting properties. Magnetic metal-organic frameworks (MMOFs) have wide applications in various fields such as drug delivery, catalyst, photocatalyst, separation, positioning, and absorption of chemical compounds [10, 11] (Scheme 1). Considering the above topics, as an attractive research future can be imagined for this class of porous magnetic compounds.



Scheme 1. Different applications of magnetic metal-organic frameworks (MMOFs).

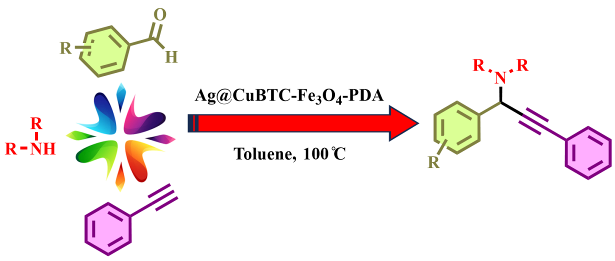
MMOFs are widely used as catalysts in chemical reactions [12]. One of the unique features of MMOFs is their high catalytic power, easy separation, and reuse, which has led to the widespread use of these materials as catalysts in chemical reactions [13]. It can be said that the high catalytic power of MMOFs is due to the synergistic properties of MOFs and Fe_3O_4 particles. MMOFs as catalysts have been shown to play an effective role in various chemical reactions such as click reaction, coupling, cycloaddition, multi-component, oxidation, photocatalyst, reduction, and Strecker reaction [14–23] (Scheme 2). Carrying out the reaction under green conditions in accordance with the principles of green chemistry, high efficiency of the synthesized products, selectivity in the reaction path, reducing the production of side products, the ability to reuse the catalyst, and the ability to separate the catalyst properly are among the advantages of using MMOFs as a catalyst in the various chemical reactions.



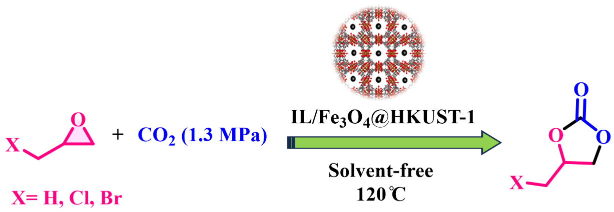
Scheme 2. Application of magnetic metal-organic frameworks (MMOFs) in different reactions.

Abstract:

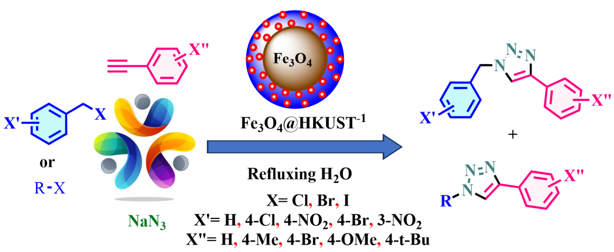
(A) Paul et al. prepared benzopyranopyrimidine derivatives by using an A^3-coupling reaction. In this research, first CuBTC-Fe_3O_4-PDA was prepared, and then Ag nanoparticles were placed on magnetic metal-organic frameworks (MMOF) above. Among the advantages of the research is the high catalytic power of Ag@CuBTC-Fe_3O_4-PDA to carry out the above reaction, which is attributed to the synergistic effects of Fe_3O_4, CuBTC, and Ag nanoparticles. Also, the high surface area of CuBTC and the uniform distribution of Ag nanoparticles are the major reasons for the high catalytic power of the desired MMOF [14].



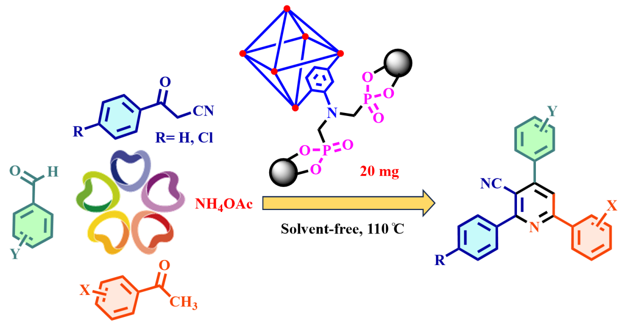
(B) In research conducted in 2021, the cycloaddition reaction of CO_2 with epoxides has been carried out under solvent-free conditions and 110 °C. In carrying out this reaction, IL/Fe_3O_4@HKUST-1 is used as a magnetic catalyst linked with ionic liquids (IL). The ability to recycle and easy separation of the catalyst from the reaction medium, the easy method of carrying out the reaction, and the high stability of the catalyst are advantages of the reported methodology [15].



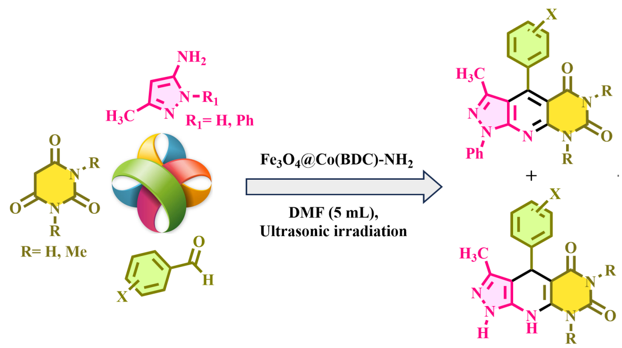
(C) In 2021, Shiri et al. have been prepared magnetic iron nanoparticles (Fe_3O_4) for synthesizing a magnetic metal-organic framework based on copper using H_3BTC and $Cu(OAc)_2$. The prepared Fe_3O_4@HKUST-1 is used for the synthesis of 1,2,3-Triazole derivatives under the click reaction. The desired reaction has been carried out in refluxing H_2O and for 90 to 180 minutes. The high efficiency of the products (80–95 %), the short reaction time, and the use of green water as a solvent are among the attractive features of the above reaction [16].



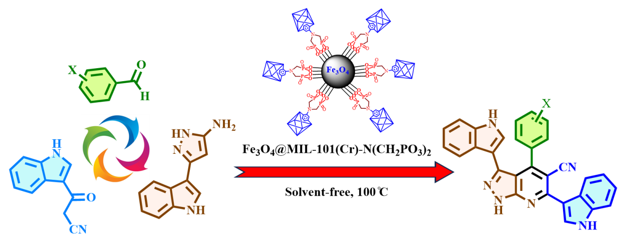
(D) In 2023, Zolfigol et al have synthesized a nano-magnetic metal-organic framework (Fe_3O_4@MIL-53(Al)-N(CH_2PO_3)$_2$). The above catalyst is used in the synthesis of nicotinonitrile derivatives under solvent-free conditions. Among the advantages of the used catalyst, it can be mentioned that it has a suitable separation capability and high chemical and thermal stability. It should be noted that Fe_3O_4@MIL-53(Al)-N(CH_2PO_3)$_2$ includes high-efficiency (68–90 %) products due to the stated features. Also, the short reaction time and the recycling ability of the catalyst are among the major features of the above research work [17].



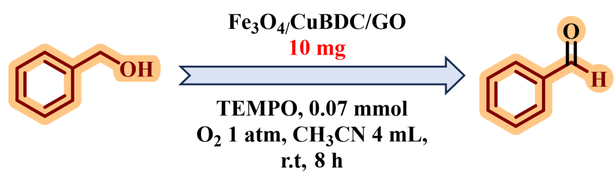
(E) In a 2021 report, Zolfigol et al. have prepared Fe_3O_4@Co(BDC)-NH_2 using magnetic iron nanoparticles (Fe_3O_4), 2-Aminoterephthalic acid (BDC-NH_2), and $Co(NO_3)_2 \cdot 6H_2O$. The above catalyst is used as a magnetic metal-organic framework (MMOFs) in the preparation of pyridines and 1,4-dihydropyridines with pyrazole and pyrimidine moieties. Examining the reaction mechanism shows that the synthesized products followed the cooperative vinylogous anomeric-based oxidation (CVABO) mechanism. The features of the above research work include the ability to easily separate the catalyst from the reaction medium, reuse of the catalyst, high reaction efficiency, and short reaction time [18].



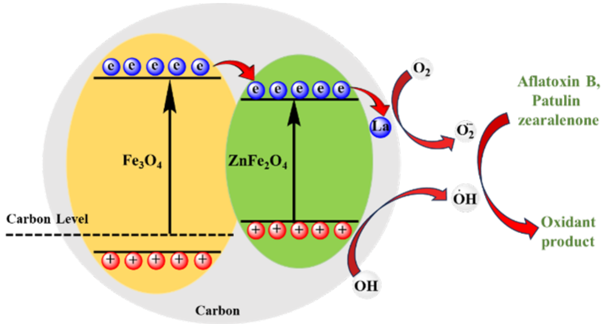
(F) In another report, MOFs based on chromium metal have been prepared and then functionalized with phosphorous acid groups (MIL-101(Cr)-N(CH_2PO_3)$_2$). In this research work, in order to increase the stability and separation capability, the above-mentioned MOFs are integrated with magnetic nanostructures (Fe_3O_4). The prepared nano-magnetic metal-organic framework has been used in a multicomponent reaction for the preparation of pyrazolo[3,4-*b*]pyridines at 100 °C under solvent-free conditions. The data from the above report shows that Fe_3O_4@MIL-101(Cr)-N(CH_2PO_3)$_2$ has a higher catalytic power compared to other organic and inorganic catalysts, and it also causes the reaction to be carried out in a shorter time [19].



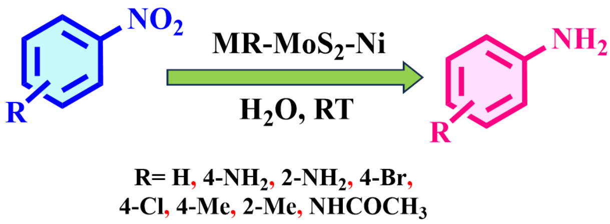
(G) Oxidation of alcohols to carbonyl compounds is an attractive branch in organic chemistry reactions. Choosing the right conditions and an efficient catalyst for the selective oxidation of alcohols is a challenge. In a research work in 2020, using Fe_3O_4/CuBDC/GO prepared from the integration of Fe_3O_4/CuBDC on graphene oxide (GO) sheets, the primary and secondary alcohols have been converted to aldehydes and ketones, respectively. This reaction is carried out under mild reaction conditions and ambient temperature with a high yield of desired products. The reusability and easy separation of the catalyst from the reaction medium are other features mentioned in the reported methodology [20].



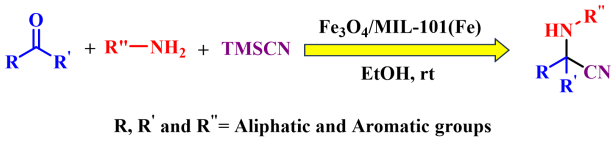
(H) Chemical pollutants have adverse effects on the environment. Nowadays, the removal of chemical pollutants has become a very interesting research topic. In 2023, Cheng et al. destroyed aflatoxin B1, patulin, and zearalenone. La-$ZnFe_2O_4$@Fe_3O_4@carbon under UV light irradiation has been used to destroy the above pollutants. The results of the mentioned work showed that pollutant aflatoxin B1, patulin, and zearalenone are destroyed with high efficiency (98 %, 97 %, and 98 %, respectively). Also, electron spin resonance analysis in this research showed that °OH and °O_2 are the radicals that cause destruction [21].



(I) In another report, Jang et al. have reduced nitro groups to their corresponding amine groups. In this work, a wide range of aromatic rings with electron-withdrawing and donating groups have been reduced to amines with excellent efficiency (93–98 %). The MR-MoS_2-Ni, prepared by placing the $NiFe_2O_4$ nanocatalyst on molybdenum disulfide (MoS_2), has been used as a catalyst in the reduction of nitro groups. The investigation shows that the above-mentioned nanocatalyst is able to perform a high-performance reduction reaction of nitro groups to amine groups under mild conditions. The reusability and easy separation of the catalyst from the reaction medium and the high efficiency of the synthesized products are attractive features of the mentioned methodology [22].



(J) In another study conducted by Movahedi et al. in 2018, Fe_3O_4/MIL-101(Fe) nanocomposite have been prepared as a magnetic metal-organic framework (MMOFs). These nanocomposites have been used as catalysts in the Strecker reaction, and a wide range of α-amino nitrile derivatives are synthesized through the three-component condensation of aldehydes (ketones), amines, and trimethylsilyl cyanide. In this study, the ability to recycle and reuse the catalyst is considered an important feature of the reported catalyst [23].



Availability of Data and Materials
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R. Du, Y. Wu, Y. Yang, T. Zhai, T. Zhou, Q. Shang, L. Zhu, C. Shang, and Z. Guo. *Adv. Energy Mater.*, **11**(2021):2100154.
DOI: https://doi.org/10.1002/aenm.202100154.

[2] L. Mao and J. Qian. *Small*, **20**(2024):2308732.
DOI: https://doi.org/10.1002/smll.202308732.

[3] B. Siu, A.R. Chowdhury, Z. Yan, S.M. Humphrey, and T. Hutter. *Coord. Chem. Rev.*, **485**(2023):215119.
DOI: https://doi.org/10.1016/j.ccr.2023.215119.

[4] Y. Peng, S. Sanati, A. Morsali, and H. García. *Angew. Chem. Int. Ed.*, **62**(2023):e202214707.
DOI: https://doi.org/10.1002/anie.202214707.

[5] S. Naghdi, M.M. Shahrestani, M. Zendehbad, H. Djahaniani, H. Kazemian, and D. Eder. *J. Hazard. Mater.*, **442**(2023):130127.
DOI: https://doi.org/10.1016/j.jhazmat.2022.130127.

[6] C. Pettinari, F. Marchetti, N. Mosca, G. Tosi, and A. Drozdov. *Polym. Int.*, **66**(2017):31–744.
DOI: https://doi.org/10.1002/pi.5315.

[7] H.D. Lawson, S.P. Walton, and C. Chan. *ACS Appl. Mater. Interfaces*, **13**(2021):7004–7020.
DOI: https://doi.org/10.1021/acsami.1c01089.

[8] S. Chu, C. Liu, X. Feng, H. Wu, and X. Liu. *Chem. Eng. J.*, **472** (2023):145159.
DOI: https://doi.org/10.1016/j.cej.2023.145159.

[9] M.R. Abdi. *Biol. Mol. Chem.*, **1**(2023):1–14.
DOI: https://doi.org/10.22034/bmc.2023.408859.1000.

[10] R. Ricco, L. Malfatti, M. Takahashi, A.J. Hill, and P. Falcaro. *J. Mater. Chem. A*, **1**(2013):13033–13045.
DOI: https://doi.org/10.1039/C3TA13140H.

[11] J. Li, R. Yao, B. Deng, Z. Li, K. Tuo, C. Fan, G. Liu, and S. Pu. *Chem. Eng. J.*, **464**(2023):142626, .
DOI: https://doi.org/10.1016/j.cej.2023.142626.

[14] S. Sharma, S. Sharma, N. Sharma, V. Sharma, and S. Paul. *New J. Chem.*, **47**(2023):4674–4686.
DOI: https://doi.org/10.1039/D3NJ00066D.

[15] T. Wang, X. Song, H. Xu, M. Chen, J. Zhang, and M. Ji. *ACS Appl. Mater. Interfaces*, **13**(2021):22836–22844, .
DOI: https://doi.org/10.1021/acsami.1c03345.

[16] E. Arefi, A. Khojastehnezhad, and A. Shiri. *Sci. Rep.*, **11**(2021): 20514.
DOI: https://doi.org/10.1038/s41598-021-00012-3.

[12] Q. Song, Y. Li, W. Xie, C. Gao, L. Liu, and B. Liu. *Sep. Purif. Technol.*, **309**(2023):122988.
DOI: https://doi.org/10.1016/j.seppur.2022.122988.

[13] S.W. Li, H.Y. Zhang, T.H. Han, W.Q. Wu, W. Wang, and J.S. Zhao. *Sep. Purif. Technol.*, **264**(2021):118460, .
DOI: https://doi.org/10.1016/j.seppur.2021.118460.

[17] B. Danishyar, H. Sepehrmansourie, H. Ahmadi, M. Zarei, M.A. Zolfigol, and M. Hosseinifard. *ACS Omega*, **8**(2023):18479–18490.
DOI: https://doi.org/10.1021/acsomega.2c06651.

[18] H. Sepehrmansourie, M. Zarei, M.A. Zolfigol, S. Babaee, and S. Rostamnia. *Sci. Rep.*, **11**(2021):5279, .
DOI: https://doi.org/10.1038/s41598-021-84005-2.

[19] H. Sepehrmansourie, M. Zarei, M.A. Zolfigol, S. Babaee, S. Azizian, and S. Rostamnia. *Sci. Rep.*, **12**(2022):14145, .
DOI: https://doi.org/10.1038/s41598-022-17879-5.

[20] H. Alamgholiloo, S. Rostamnia, K. Zhang, T.H. Lee, Y.S. Lee, R.S. Varma, H.W. Jang, and M. Shokouhimehr. *ACS Omega*, **5**(2020): 5182–5191.
DOI: https://doi.org/10.1021/acsomega.9b04209.

[21] X. Yang, J. Pan, J. Hu, S. Zhao, and K. Cheng. *Chem. Eng. J.*, **467** (2023):143381.
DOI: https://doi.org/10.1016/j.cej.2023.143381.

[22] J. Wang, J. Kim, J. Bu, D. Kim, S.Y. Kim, K.T. Nam, R.S. Varma, H.W. Jang, R. Luque, and M. Shokouhimehr. *J. Ind. Eng. Chem.*, **107**(2022):428–435, .
DOI: https://doi.org/10.1016/j.jiec.2021.12.013.

[23] M.M. Mostafavi and F. Movahedi. *Appl. Organomet. Chem.*, **32** (2018):e4217.
DOI: https://doi.org/10.1002/aoc.4217.