RSC Mechanochemistry



PAPER

View Article Online



Cite this: RSC Mechanochem., 2025, 2,

with pre-designed mixed metal clusters†

isoreticular flexible metal-organic frameworks

A mechanochemical synthetic strategy of

Mechanochemistry has emerged as a sustainable alternative to traditional solvothermal methods for synthesizing metal-organic frameworks (MOFs), offering reduced solvent usage, shorter reaction times, and scalability. However, the synthesis of flexible MOFs, such as the MIL-88 series, remains challenging due to the difficulty in forming secondary building units (SBUs) under mechanochemical conditions. Herein, we present a novel strategy for the mechanochemical synthesis of the MIL-88 series using preassembled mixed-metal clusters as precursors. This approach effectively overcomes limitations in controlling metal ratios and suppressing undesired phase mixtures, enabling the efficient and rapid formation of MIL-88 frameworks under mild conditions. The synthesized MIL-88s, including mixedmetal variants, were comprehensively characterized to confirm phase purity, structural fidelity, and tunable metal compositions. This strategy not only facilitates access to flexible MOFs that were previously difficult to synthesize mechanochemically but also demonstrates the feasibility of precisely controlling metal ratios in mixed-metal systems. These advancements underscore the significant potential of this approach for further expanding the scope and applications of mechanochemical synthesis.

Received 13th January 2025 Accepted 15th February 2025

DOI: 10.1039/d5mr00010f

rsc.li/RSCMechanochem

Introduction

Among the various synthetic methods of metal-organic frameworks (MOFs),1 mechanochemistry has emerged as a sustainable alternative to traditional solvothermal and hydrothermal approaches.2 It offers significant advantages, including reduced solvent usage, shorter reaction times, scalability, and alignment with green chemistry principles.3-6 Mechanochemical methods have successfully synthesized well-known MOFs such as MOF-74,7 MOF-5,8 UiO-66,9 HKUST-1,10 and ZIF-8,11 highlighting their potential in MOF synthesis. 12-14 However, synthesizing flexible MOFs via mechanochemistry remains a challenge. For MOFs like MIL-88 and MIL-53, conventional mechanochemical methods typically require additional solvothermal steps after grinding, which diminishes the environmental and operational benefits of mechanochemistry.¹⁵⁻¹⁷ Recently, the isoreticular MIL-53 series was successfully synthesized without additional heating steps by employing basic modulators such as sodium hydroxide.18 This method was effective not only for aluminiumbased MIL-53 but also for gallium- and indium-based analogues. In contrast, the direct mechanochemical synthesis of MIL-88 remains difficult. This challenge arises from the inherent complexity of forming $M_3(\mu_3-O)$ clusters - the secondary building units (SBUs) of MIL-88 - under mechanochemical conditions.15 Unlike their well-established solvothermal synthesis, the mechanochemical synthesis of the clusters has not been reported, limiting the diversity of MOFs accessible through this approach.19-21

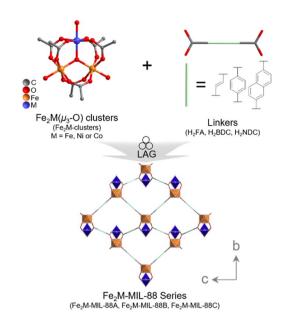
To overcome these challenges, this study employs preassembled M₃(µ₃-O), as tailored precursors for the direct mechanochemical synthesis of flexible MOFs (Scheme 1). The use of pre-synthesized cluster as a precursor has previously been demonstrated for the synthesis of Zr-based MOFs, a challenging series due to the difficulty of forming Zr SBUs under mechanochemical conditions.22-25 This approach provided the rapid and efficient synthesis of Zr-based MOFs through direct mechanochemical reactions.

Building on this concept, we demonstrate the successful mechanochemical synthesis of the MIL-88 series, achieving efficient production of flexible MOFs without post-treatment. Moreover, this strategy extends to the synthesis of multivariate MIL-88s with mixed-metal cluster systems, incorporating combinations of nickel (Ni) or cobalt (Co) with iron (Fe). Conventional one-pot solvothermal synthesis of mixed-metal MOFs often struggles to control metal ratios and is prone to forming undesired mixed phases.26 In contrast, our approach offers a fast and straightforward method to precisely control metal ratios while suppressing phase impurities, ensuring the formation of targeted structures. Finally, the scalability and

^aDepartment of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

^bDepartment of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Republic of Korea. E-mail: hoirimoon@ehwa.ac.kr

[†] Electronic supplementary information (ESI) available. See https://doi.org/10.1039/d5mr00010f



Scheme 1 Schematic representation of the mechanochemical synthesis of the Fe₂M-MIL-88 series using pre-designed mixed metal clusters and organic linkers.

adaptability of this method are showcased through the successful synthesis of isoreticular MIL-88A, MIL-88B, and MIL-88C.

Experimental

Materials and characterization methods

All reagents are commercially available (Sigma Aldrich, TCI, Dae Jung, and Samchun) and used without any purification. All metal clusters were synthesized by modifying previously reported methods.27 Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 phaser diffractometer at 10 mA and 30 kV for Cu K α (wavelength = 1.5406 Å), with a 0.02 degree of increment. Thermogravimetric analysis (TGA) was performed under nitrogen (N_2) flow at a ramp rate of 10 °C min⁻¹, using a TA instruments TGA Q50. Fourier-transform infrared spectra (FT-IR) and diffuse reflectance infrared Fourier-transform (DRIFT) spectra were measured with a ThermoFisher Scientific iS10 FT-IR spectrometer. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed with a JEOL JSM-7610 at the Basic Science Research Institute of Ewha Womans University. N2 (77 K) sorption data were collected using a Microtrac BEL Corp BELSORP-max. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed with an Agilent 5110 at the Yonsei Center for Research Facilities of Yonsei University. Mechanochemical reactions were conducted with a Retsch MM400 shaker mill. All mechanochemical reactions were achieved by milling for 90 min at a rate of 30 Hz in a 15 mL Teflon jar with two 7 mm steel balls.

Synthesis of Fe₃-cluster ([Fe₃(μ_3 -O)(OAc)₆(H₂O)₃][Fe₃(μ_3 -O) $(OAc)_{7.5}$ ₂·7H₂O). Sodium acetate (8.16 g, 0.06 mol) and FeCl₃-·6H₂O (8.11 g, 0.03 mol) were dissolved in 10 mL of hot deionized water. Sodium and iron solutions were combined and

stirred for 10 min. The mixed solution was left and exposed to air for crystallization. After several days, the crystals were filtered and washed with small amounts of ethanol (EtOH) and diethyl ether. The product was dried in the air.

Synthesis of Fe₂Co-cluster ([Fe₂Co(μ₃-O)(OAc)₆(H₂O)₃]) and Fe_2Ni -cluster ($[Fe_2Ni(\mu_3-O)(OAc)_6(H_2O)_3]$). Sodium acetate (12.31 g, 0.15 mol), Fe(NO₃)₃·9H₂O (2.42 g, 0.01 mol) and $Co(NO_3)_2 \cdot 6H_2O$ (8.73 g, 0.03 mol) (or $Ni(NO_3)_2 \cdot 6H_2O$ (8.72 g, 0.03 mol)) were dissolved in 10 mL of deionized water. The mixed solutions were stirred for 24 h at RT. The product was washed with a small amount of water and EtOH. The product was dried under vacuum at RT.

Synthesis of Fe₃-MIL-88B. Fe₃-cluster (179.0 mg, 0.1 mmol) and terephthalic acid (H₂BDC) (149.4 mg, 0.9 mmol) were milled with 140 µL of methanol (MeOH) and 40 µL of N,N-diisopropylethylamine (DIPEA). The product was washed with MeOH and N,N-dimethylformamide (DMF). The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Synthesis of Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B. Fe₂Cocluster (115.4 mg, 0.2 mmol) or Fe₂Ni-cluster (115.3 mg, 0.2 mmol), H₂BDC (99.6 mg, 0.6 mmol) were milled with 150 µL of MeOH and DIPEA mixed solution in a 7:2 ratio. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Synthesis of Fe₃-MIL-88A. Fe₃-cluster (179.0 mg, 0.1 mmol), fumaric acid (H₂FA) (104.5 mg, 0.9 mmol) were milled with 120 μL of EtOH and 30 μL of DIPEA. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Synthesis of Fe₂Co-MIL-88A and Fe₂Ni-MIL-88A. Fe₂Cocluster (173.1 mg, 0.3 mmol) or Fe₂Ni-cluster (173.0 mg, 0.3 mmol), H₂FA (104.5 mg, 0.9 mmol) were milled with 120 µL of EtOH and 30 µL of DIPEA. The product was washed with MeOH and DMF. The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Synthesis of Fe₃-MIL-88C. Fe₃-cluster (179.0 mg, 0.1 mmol) and 2,6-naphthalenedicarboxylic acid (H2NDC) (194.5 mg, 0.9 mmol) were milled with 50 µL of MeOH and 20 µL of DIPEA. The product was washed with DMF. The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Synthesis of Fe₂Co-MIL-88C and Fe₂Ni-MIL-88C. Fe₂Cocluster (173.1 mg, 0.3 mmol) (or Fe₂Ni-cluster (173.0 mg, 0.3 mmol)) and H₂NDC (194.5 mg, 0.9 mmol) were milled with 50 μL of MeOH and 20 μL of DIPEA. The product was dried with vacuum filtration and obtained after drying in a 65 °C vacuum oven overnight.

Results and discussion

As the first synthetic step of MIL-88 series, we prepared the trimeric clusters, M₃(µ₃-O), capped with six acetate groups (OAc), which act as SBU precursors in the synthesis of MOFs. Following previously reported methods,27 sodium acetate and metal nitrate hydrates were dissolved in deionized water to

produce three types of crystalline metal clusters: [Fe₃(µ₃-O)(OAc)₆(H₂O)₃][Fe₃(μ_3 -O)(OAc)_{7.5}]₂·7H₂O (Fe₃-cluster), $[Fe_2Co(\mu_3-O)(OAc)_6(H_2O)_3]$ (Fe_2Co-cluster), and [Fe₂Ni(µ₃-O)(OAc)₆(H₂O)₃] (Fe₂Ni-cluster). Notably, the Fe₃-cluster, which had a different formula compared to the Fe₂Co-cluster and Fe₂Ni-cluster, exhibited a network structure rather than discrete clusters; however, the $M_3(\mu_3$ -O) core remained identical. The synthesized clusters were characterized using DRIFT spectroscopy, SEM-EDX, ICP-OES, and PXRD. DRIFT spectroscopy showed distinct asymmetric stretching bands (730 cm⁻¹ for Fe₂Ni-cluster, 725 cm⁻¹ for Fe₂Co-cluster) absent in the Fe₃cluster, confirming mixed-metal incorporation (Fig. 1 and Table S1†).28,29 EDX and ICP-OES confirmed a approximately 2:1 molar ratio of iron to nickel or cobalt in the mixed-metal clusters (Fig. S1†). PXRD patterns of three clusters were matched with previously reported data, verifying the same packing structures of $M_3(\mu_3-O)$ clusters (Fig. S2†). 30,31 These results demonstrate the successful synthesis of mixed-metal trimeric clusters, enabling the development of MIL-88s.

The synthesis of MIL-88B, the most extensively studied MOF in this series, featuring the BDC ligand, was investigated first. The mechanochemical conditions for MIL-88B were optimized based on a previously reported solvothermal method utilizing metal clusters. In this mechanochemical synthesis, MeOH was added as an additive liquid for liquid-assisted grinding (LAG). DIPEA was also introduced for a dual purpose as a base for the MOF formation and as a liquid for LAG. For MIL-88B with Fe₃ clusters (Fe₃-MIL-88B), the optimized synthesis involved milling 0.1 mmol of Fe₃-clusters and 0.9 mmol of H_2BDC with 140 μL of MeOH and 40 µL of DIPEA. For mixed-metal MIL-88B containing cobalt or nickel (Fe₂Co-MIL-88B or Fe₂Ni-MIL-88B), 0.2 mmol of Fe₂Co or Fe₂Ni clusters and 0.6 mmol of H₂BDC were milled with 150 μL of a solvent mixture MeOH and DIPEA in a 2:7 ratio. All mechanochemical reactions were conducted at 30 Hz for 90 min in a 15 mL Teflon jar containing two 7 mm stainless steel balls. The products were isolated using MeOH and further washed with MeOH and DMF. Compared to

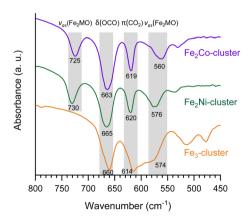


Fig. 1 DRIFT spectra of Fe₃-cluster, Fe₂Ni-cluster, and Fe₂Co-cluster. Asymmetric stretching bands at 730 cm⁻¹ for Fe₂Ni-cluster and 725 cm⁻¹ for Fe₂Co-cluster, which were absent in the Fe₃-cluster. Asymmetric stretching bands were originated from the degeneracy of asymmetric vibration of Fe₂M(μ ₃-O) moiety resulting from geometry reduction from D_{3h} to C_{2v} .

solvothermal methods, which require over a day of reaction time, the mechanochemical approach significantly shortens the process to just 90 min while still achieving the successful synthesis of MIL-88B.

To confirm the successful synthesis of MIL-88Bs, the PXRD patterns were collected after isolating from DMF. The observed patterns were well matched with the calculated pattern of the open structure of MIL-88B (Fig. 2a).32 Further detailed characterization was performed on the MIL-88B series for comprehensive analysis. FT-IR spectra confirmed the coordination between the deprotonated organic linkers and the metal clusters, as evidenced by asymmetric and symmetric vibrations of the carboxylate groups (Fig. S3†). Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B exhibited distinct asymmetric stretching bands at approximately 715 cm⁻¹, absent in Fe₃-MIL-88B. It indicated that Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B were well-constructed with mixed metal cluster systems (Fig. S4†).33-35 This was further confirmed through EDX analysis, which revealed that Fe and Co or Ni were present in Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B at an approximate molar ratio of 1:2 (Fig. S5†). TGA showed that all MIL-88Bs displayed an initial weight loss below 200 °C, corresponding to the removal of guest molecules, followed by a second weight loss around 350 °C, attributed to the framework degradation (Fig. S6†). The N2 sorption measurements of MIL-88Bs exhibited the type 2 isotherm, indicating their non-

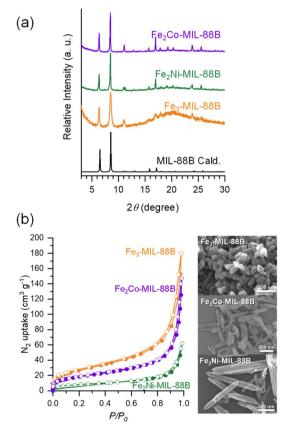


Fig. 2 (a) PXRD patterns of Fe $_3$ -MIL-88B, Fe $_2$ Co-MIL-88B, and Fe $_2$ Ni-MIL-88B collected after isolation from DMF. (b) N $_2$ isotherms at 77 K and SEM images of Fe $_3$ -MIL-88B, Fe $_2$ Co-MIL-88B, and Fe $_2$ Ni-MIL-88B.

porous and non-flexible nature toward N2 (Fig. 2b).27 This behavior is attributed to the dense phase of dried MIL-88Bs, which maintains narrow pores upon N2 adsorption. The nitrogen uptake was observed to decrease in the order of Fe₃-MIL-88B, Fe₂Co-MIL-88B, and Fe₂Ni-MIL-88B, suggesting that the introduction of a mixed-metal system affects the dried structure. One possible explanation is the presence of a coordinating anion in Fe₃-MIL-88B, which is absent in the M²⁺-containing Fe₂Co-MIL-88B and Fe₂Ni-MIL-88B. However, further investigation is still required to fully understand this phenomenon.

To compare the products synthesized mechanochemically to their solvothermal counterparts, Fe₃-MIL-88B was synthesized using a previously reported solvothermal method with preassembled iron clusters. The PXRD pattern of Fe₃-MIL-88B synthesized via the solvothermal reaction (Fe₃-MIL-88B-Solvo) was identical to that of the mechanochemically synthesized Fe₃-MIL-88B (Fig. S7†).³⁶ The textural properties of Fe₃-MIL-88B and Fe₃-MIL-88B-Solvo were studied with N₂ sorption isotherms measured at 77 K (Fig. 2b and S8†). At the low pressure region, both Fe₃-MIL-88B and Fe₃-MIL-88B-Solvo exhibited similar sorption behavior. However, at higher relative pressures (0.8-1.0), Fe₃-MIL-88B demonstrated greater nitrogen uptake compared to Fe3-MIL-88B-Solvo. This behavior was likely influenced by the difference in crystal sizes between the two samples. SEM images revealed that Fe₃-MIL-88B-Solvo featured microcrystals with an average size exceeding 5 μm, whereas Fe₃-MIL-88B displayed smaller nanocrystals with an average size of around 100 nm (Fig. 2b and S9†). The nano-sized crystals of Fe₃-MIL-88B might contribute to the presence of intercrystalline voids, resulting in mesoporosity.37 Overall, these results confirm the successful mechanochemical synthesis of the MIL-88B series with properties comparable to solvothermal MIL-88Bs. Therefore, the well-designed mechanochemical strategy, with its shorter reaction time and higher yield, offers greater efficiency and presents a promising alternative to the solvothermal method.

To extend our strategy, we attempted to synthesize the isoreticular series of MIL-88B, MIL-88A and MIL-88C. The mechanochemical syntheses of Fe₃-MIL-88A, Fe₂Co-MIL-88A, and Fe₂Ni-MIL-88A were processed with H₂FA under the similar conditions with MIL-88B syntheses. The successful synthesis of series of MIL-88A was confirmed with the PXRD patterns of these materials by comparing with the calculated patterns of MIL-88A (Fig. 3a). While Fe₃-MIL-88A exhibited slight deviations from the calculated patterns, this was attributed to the small crystal size, approximately 50 nm, which caused peak broadening, as well as the inherent flexibility of MIL-88A. In contrast, Fe₂Co-MIL-88A and Fe₂Ni-MIL-88A displayed crystal sizes of approximately 500 nm, as observed in SEM images, and exhibited the characteristic spindle-like morphology commonly associated with MIL-88A. Additionally, the minor peaks observed below 10° in all three MOFs resulted from air exposure during PXRD measurements, which caused a slight transition from the dried phase to a partially open phase. This phenomenon is commonly observed in previously reported MIL-88A samples.38 To confirm the incorporation of mixed metals into Fe₂Co-MIL-88A and Fe₂Ni-MIL-88A,

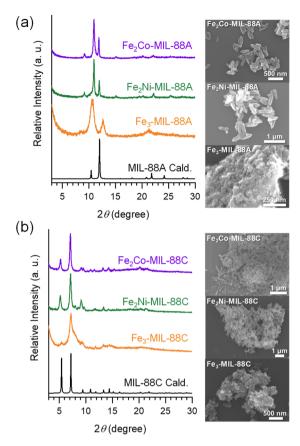


Fig. 3 (a) PXRD patterns and SEM images of Fe₂Co-MIL-88A, Fe₂Ni-MIL-88A, and Fe₃-MIL-88A after drying. (b) PXRD patterns and SEM images of Fe₂Co-MIL-88C, Fe₂Ni-MIL-88C, and Fe₃-MIL-88C after drying.

EDX analysis was conducted, revealing molar ratio of Fe and Co or Ni in approximately 2:1 within the frameworks (Fig. S10†). Furthermore, consistent with the observation in MIL-88B, the FT-IR spectra displayed a characteristic band at 730 cm⁻¹, attributed to the incorporation of mixed-metal clusters (Fig. S11†). These results conclusively demonstrate the successful synthesis of MIL-88A and validate the effectiveness of the proposed strategy for designing isoreticular MOFs. Furthermore, this approach could be extended to MIL-88C, which features a longer and symmetrically mismatched linker (H2NDC). The synthetic conditions for MIL-88C are identical to those for MIL-88A, and the only differences lie in the amount of liquid additives. Comprehensive characterization using PXRD, SEM, EDX, and FT-IR confirmed the successful synthesis of MIL-88C (Fig. 3b and S12†).

Conclusions

In this study, we introduced a mechanochemical strategy for synthesizing the MIL-88 series, using pre-assembled mixedmetal clusters. This approach effectively addresses the challenges associated with constructing SBUs under mechanochemical conditions. By utilizing these pre-designed clusters, we successfully synthesized MIL-88A, MIL-88B, and MIL-88C with precise control over metal ratios and phase purity, even in mixed-metal systems. The synthesized MOFs exhibited

structural and functional properties comparable to those obtained *via* traditional solvothermal methods, while providing significant advantages such as shorter reaction times and reduced solvent use. Furthermore, this approach enables the precise introduction of well-regulated mixed-metal systems into MOFs by controlling the metal ratios in mixed-metal clusters. This method reduces the formation of side products commonly observed in conventional salt-based solvothermal or mechanochemical syntheses of mixed-metal MOFs. These findings demonstrate the high scalability of the mechanochemical strategy employing pre-designed clusters for the rational design and synthesis of isoreticular MOFs. We believe it will open new possibilities for accessing novel MOF structures and broadening the scope of mechanochemical MOF synthesis.

Data availability

All data generated or analyzed during this study are included in this published article and the ESI. \dagger

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was financially supported by the National Research Foundation of Korea (NRF) grants (2020R1A2C3008908) and Korean Basic Science Institutes (National Research Facilities and Equipment Center) grant funded by the Ministry of Education (2020R1A6 C101B194).

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