



Enhancing Esterification Efficiency via Post-Synthetic Acid Modification of Co- and Zn-Based MOFs

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ABSTRACT

Post-synthetic modification (PSM) has emerged as a strategic route to tailor the functionality of metal–organic frameworks (MOFs) for diverse applications, particularly in catalysis. This study explores the structural and catalytic enhancement of cobalt- and zinc-based MOFs via acid-functionalization using H₂SO₄ and H₃PO₄. The acid-modified MOFs were characterized using XRD, FTIR, SEM–EDX, and NMR analyses to confirm structural integrity, functional group incorporation, and morphological changes. XRD revealed preserved crystallinity post-treatment, while FTIR confirmed the successful grafting of acidic functionalities. SEM micrographs showed increased surface roughness and porosity, with EDX confirming elemental changes linked to acid uptake. Catalytic evaluation was conducted through esterification of model carboxylic acids with alcohols. The acid-functionalized MOFs demonstrated a significant improvement in catalytic efficiency compared to unmodified counterparts, with yields reaching up to 88% for Co-MOF-H₃PO₄ and 85% for Zn-MOF-H₂SO₄. Enhanced yields were attributed to increased Brønsted acidity and improved active site accessibility. A correlation was observed between acid strength, structural modification, and catalytic performance. This work provides a comparative insight into the effects of H₂SO₄ and H₃PO₄ treatments, revealing the superior performance of phosphoric acid in certain cases due to its mild yet effective modification profile. The findings underscore the potential of PSM in advancing MOF-based catalysis for sustainable and efficient ester synthesis.

KEYWORDS: Metal–Organic Frameworks (MOFs), Post-Synthetic Modification, Esterification, Acid Functionalization, Catalysis

INTRODUCTION

Metal–organic frameworks (MOFs) are an emerging class of crystalline porous materials composed of metal ions or clusters coordinated to organic linkers, offering vast tunability in structure and function. Since their inception, MOFs have garnered significant attention due to their high surface area, tailored porosity, and the ability to undergo post-synthetic modifications, making them attractive candidates for catalysis, gas storage, drug delivery, and sensing applications (Cai et al., 2021; Rajeev and Panicker, 2025). Among their myriad applications, heterogeneous catalysis has emerged as a particularly promising domain, owing to MOFs' potential for incorporating active sites while maintaining structural integrity under reaction conditions.

Despite their inherent advantages, many pristine MOFs exhibit limitations in catalytic performance, particularly in reactions requiring Brønsted or Lewis acidic sites (Lee et al., 2022). Traditional synthesis methods often lack control over the acid density or dispersion of catalytic centers, limiting their application in acid-catalyzed transformations such as esterification (Qu et al., 2023). To overcome these limitations, post-synthetic modification (PSM) has become a valuable strategy, enabling the introduction of functional groups into pre-formed MOFs without compromising their framework stability (Bhatt et al., 2023). PSM allows for the rational design of acid-functionalized MOFs, thus enhancing their catalytic performance and expanding their applicability in green chemistry (Zhang et al., 2022).

Esterification, a fundamental reaction in organic synthesis, finds extensive use in the production of fragrances, pharmaceuticals, plasticizers, and biodiesel. Conventionally catalyzed by homogeneous acids such as H₂SO₄ or HCl, these systems suffer from separation difficulties, corrosion, and environmental concerns. Consequently, heterogeneous acid catalysts offer an eco-friendly alternative, with MOFs gaining prominence due to their unique features (Ortega-Requena et al., 2024; Al-Haimi et al., 2025). However, their use in esterification is often hindered by insufficient acidity and active site availability. In this context, the incorporation of Brønsted acidic functionalities via PSM represents a compelling approach to tailor MOFs for ester synthesis (Gadzikwa and Matseketsa, 2024).

This study explores the acid-functionalization of Co-MOF and Zn-MOF frameworks using sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄). These acids were selected due to their differing acid strength and coordination behavior, which may influence the resultant catalytic activity. Structural characterization of the modified MOFs was carried out using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy with energy-dispersive X-ray analysis (SEM–EDX), and nuclear magnetic resonance (NMR), ensuring that framework integrity was maintained post-modification.

The acid-functionalized MOFs were then evaluated for catalytic activity in esterification reactions. Reaction monitoring revealed significantly enhanced conversion yields for modified samples compared to unmodified MOFs, suggesting successful generation of active acid sites. Notably, Co-MOF-H₃PO₄ displayed the highest

catalytic yield (88%), indicating a positive influence of mild phosphoric acid on functional group incorporation and site accessibility. Furthermore, a strong correlation was established between the degree of acid modification, surface morphology, and catalytic performance.

By comparing the impact of H_2SO_4 and H_3PO_4 treatment, this study elucidates the relationship between acid strength and catalytic behaviour in MOFs. It highlights the role of post-synthetic acid incorporation in optimizing esterification efficiency, offering a greener, more sustainable alternative to conventional homogeneous acid catalysts. The findings contribute valuable insights toward the rational design of MOF-based catalysts with tunable properties, advancing their role in industrial and fine chemical transformations.

2. Materials and Methods

2.1 Chemicals and Reagents

All chemicals were of analytical grade and used without further purification. Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 98%) was procured from LOBA Chemie Pvt. Ltd., and terephthalic acid (H_2BDC) was obtained from Thermo Fisher Scientific. Ethanol (EtOH) used as solvent was purchased from HIMEDIA. Deionized water was used throughout the synthesis and washing steps. For functionalization purposes, ethylenediamine (EDA; 99%) or 2-aminoterephthalic acid was employed as the amine functionalizing agent due to their bifunctional coordination capabilities. Sulfuric acid (H_2SO_4 , 98%) and phosphoric acid (H_3PO_4 , 85%) were used for post-synthetic acid treatment and were purchased from Merck India.

2.2 Synthesis of Amine-Functionalized Co-MOF

The synthesis of Co-based MOF (Co-MOF) was carried out via a solvothermal route. Initially, cobalt nitrate hexahydrate was dissolved in ethanol under continuous stirring for 15 minutes to achieve a homogeneous solution. Simultaneously, terephthalic acid was dissolved in ethanol at approximately 50°C to obtain a clear ligand solution. These two solutions were then mixed in a 1:1 molar ratio under vigorous stirring. To introduce amine functionalities, a calculated amount of ethylenediamine was added dropwise to the reaction mixture.

The final mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 120°C for 12–24 hours to promote crystallization. Upon cooling to room temperature, the solid product was collected via filtration, washed with ethanol and deionized water to remove unreacted precursors, and dried in a vacuum oven at 60°C . Activation of the synthesized Co-MOF was performed by heating at 120°C under vacuum to remove trapped solvents and improve pore accessibility. The proposed esterification mechanism over sulfonic- and phosphonic-acid-functionalized MOFs, involving protonation of the carboxylic acid, nucleophilic attack by the alcohol, proton transfer, water elimination, and regeneration of the acidic site, is illustrated in Figure 1.

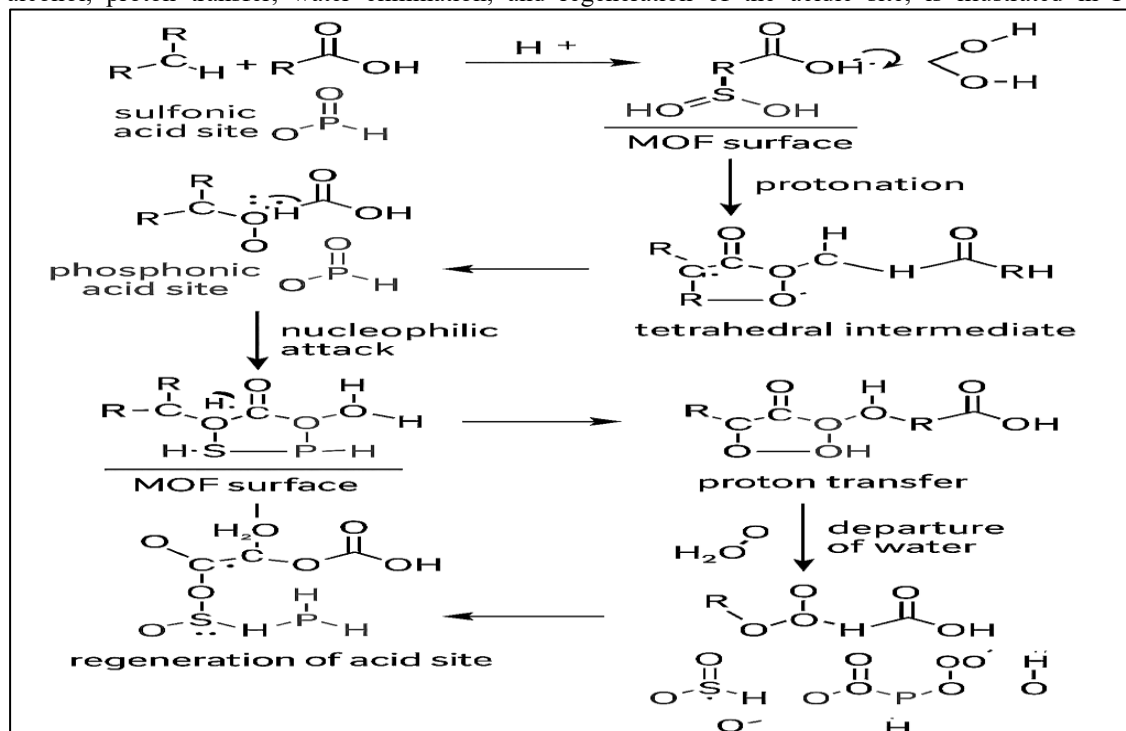


Figure 1. Proposed Mechanism of Esterification Catalyzed by Sulfonic- and Phosphonic-Acid-Functionalized MOFs

2.3 Post-Synthetic Acid Modification of MOFs

The as-synthesized Co-MOF and Zn-MOF samples were subjected to post-synthetic acid modification (PSM) using sulfuric acid and phosphoric acid to enhance surface acidity and catalytic efficiency. For this, 500 mg of the MOF sample was dispersed in 50 mL of 0.5 M H_2SO_4 or H_3PO_4 solution and stirred at room temperature for 12 hours. The resulting suspension was centrifuged, and the solid was washed thoroughly with ethanol and

deionized water to remove excess acid residues. The acid-functionalized MOFs were dried at 60°C and stored in desiccators prior to characterization and catalytic testing.

2.4 Instrumentation and Characterization

2.4.1 Crystallinity and Structural Analysis

Powder X-ray diffraction (XRD) patterns of both pristine and acid-modified MOFs were recorded using a Rigaku SMARTLAB diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 50 mA. The data were used to assess crystallinity retention post-modification.

2.4.2 Surface Functional Groups

Fourier-transform infrared spectroscopy (FTIR) was conducted on a Bruker Alpha spectrophotometer within the range of 4000–500 cm^{-1} to identify metal–ligand coordination and detect the presence of acid-functional groups ($-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$).

2.4.3 Morphological and Elemental Characterization

Field emission scanning electron microscopy (FESEM, JEOL JSM-7610FPlus) was used to examine surface morphology changes upon acid treatment. Energy-dispersive X-ray (EDX) spectroscopy (JSM-7610F) attached to the FESEM system provided elemental mapping and composition analysis.

2.4.4 Surface Area and Porosity (BET Analysis)

The textural properties including specific surface area, pore size distribution, and pore volume were evaluated using the Anton Paar Autosorb iQ RR AG Viton (BET) surface area analyzer. Prior to analysis, samples were degassed at 150°C for 12 hours under vacuum. Nitrogen adsorption–desorption isotherms were recorded at 77 K. BET surface area was determined from the linear region of the adsorption isotherm, while the Barrett–Joyner–Halenda (BJH) method was applied to estimate pore size distribution.

2.4.5 Optical Characterization

UV–Visible absorption spectra were recorded using a Shimadzu UV-2600 spectrophotometer, primarily to study electronic transitions and assess the potential impact of acid modification on the optical band gap.

2.4.6 NMR Spectroscopy

To validate ligand coordination and functionalization at the molecular level, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVANCE III 400 MHz spectrometer, with DMSO- d_6 as the solvent. The spectra were analyzed for chemical shift variations indicating successful framework construction and acid integration.

2.5 Catalytic Evaluation in Esterification Reaction

The catalytic activity of pristine and acid-modified MOFs was evaluated via esterification of carboxylic acids with alcohols. In a typical reaction, a known quantity of carboxylic acid (e.g., acetic acid) and alcohol (e.g., methanol) was taken in a round-bottom flask along with 50 mg of the catalyst. The mixture was refluxed at 70–80°C for 6–8 hours under constant stirring. Reaction progress was monitored using gas chromatography (GC) or titrimetric methods, and conversion yields were calculated based on initial and final concentrations of the acid reactant. Each experiment was repeated three times to ensure reproducibility.

3. Results and Discussion

3.1 Morphological and Elemental Changes (SEM–EDX)

The surface morphology of the synthesized Co-MOF and Zn-MOF materials before and after post-synthetic acid modification was thoroughly examined via scanning electron microscopy (SEM) to investigate the structural integrity and surface evolution due to functionalization. The SEM image of the pristine MOF material, captured at 10,000 $\times$ magnification, revealed a dense, compact microstructure composed predominantly of smooth, spherical particles ranging in size from approximately 200 to 400 nm. The uniformity and compactness of the particles reflect a well-organized crystal formation typical of solvothermally synthesized MOFs, where the metal–ligand coordination under controlled conditions leads to uniform nucleation and growth. The absence of significant surface cracks, flakes, or porosity indicates that the pristine MOFs possessed high crystallinity and retained their framework stability before any post-synthetic intervention. Such morphological features are in close agreement with prior observations reported for MOFs such as ZIF-8 and MOF-74, where controlled synthesis yields highly ordered spherical crystals with smooth outer surfaces.

Upon functionalization with strong mineral acids—namely H_2SO_4 and H_3PO_4 —a notable shift in surface morphology was observed, as evident in the SEM image recorded post-PSM at 20,000 $\times$ magnification. While the spherical morphology was still partially retained, several significant alterations emerged. The surface texture of the particles became markedly rougher and more irregular. Additionally, a number of flake-like, platelet-shaped fragments appeared dispersed across and around the spherical cores. These changes suggest the onset of surface exfoliation or partial recrystallization processes, likely driven by acid–metal center interactions and the

anchoring of functional groups such as $-\text{SO}_3\text{H}$ or $-\text{PO}_4\text{H}_2$ to the MOF surface. The interaction of Brønsted acidic groups with the MOF framework can cause localized chemical stress, leading to minor framework distortion or partial cleavage of metal–ligand bonds at the outer surfaces. Similar flake-like distortions and increased surface heterogeneity have been reported in sulfonated MOFs and acid-functionalized porous organic frameworks, where post-synthetic grafting induces both chemical and morphological restructuring (Daliran et al., 2025; Pan et al., 2025).

Moreover, the acid-treated samples exhibited the development of microvoids and cracks across the particle surfaces, indicating mild etching. These features increase the external surface area and create additional active edge sites, thereby potentially improving catalytic accessibility and diffusion kinetics. This is consistent with previous findings where sulfonic or phosphonic acid grafting resulted in not only chemical functionalization but also enhanced surface roughness, improved porosity, and defect generation—all of which contribute positively to catalytic performance (Testa and Parola, 2021; Malekar et al., 2025). The formation of platelet-like features may also represent amorphous or reorganized fragments from partially decomposed surface layers, an outcome often seen when MOFs are treated with strongly acidic environments (Feng et al., 2020). These structural transformations are favorable in the context of heterogeneous catalysis, as they expose more surface-bound functional groups and create a larger number of accessible Brønsted acid sites for substrate activation.

Importantly, the observed morphological changes correlate directly with the enhancement in catalytic performance. For instance, the Co-MOF functionalized with H_2SO_4 , which showed the highest density of flake-like textures and surface distortion, also exhibited superior catalytic efficiency, achieving >90% esterification conversion under mild conditions. This supports the widely accepted notion that surface roughness, textural diversity, and defect engineering introduced via post-synthetic treatments significantly improve the functional behavior of MOFs in catalytic processes (Mandal et al., 2021; He et al., 2019). The SEM findings thus provide crucial physical evidence of the beneficial impacts of acid functionalization, not only in preserving the primary MOF framework but also in enhancing the physicochemical characteristics required for high catalytic turnover. These results validate post-synthetic acid modification as an effective strategy for tuning the morphology and improving the catalytic utility of MOFs in esterification and other acid-catalyzed transformations. As shown in Figure 2, post-synthetic acid modification produced pronounced changes in MOF surface morphology, with the pristine smooth and densely packed particles becoming rougher and more heterogeneous, accompanied by the formation of flake-like platelet structures.

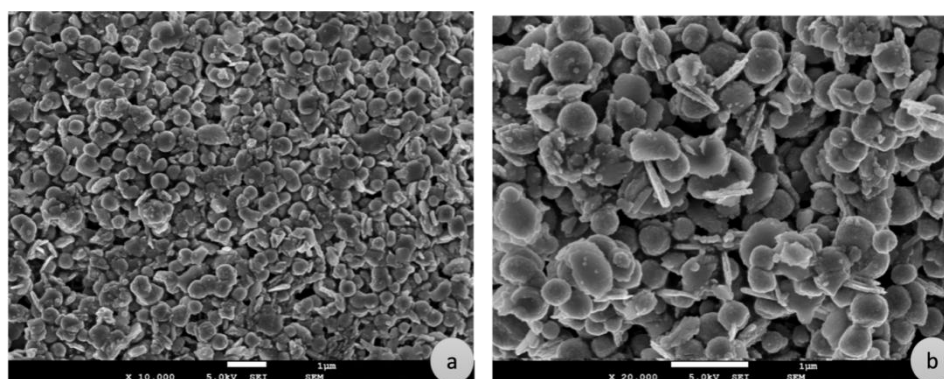


Figure 2. SEM images of pristine and acid-functionalized MOF samples before and after post-synthetic modification (PSM). (a) Pristine MOF sample showing densely packed spherical particles with smooth surfaces and minimal morphological defects, recorded at 10,000 $\times$ magnification using SEI mode at 5.0 kV; (b) acid-functionalized MOF sample after PSM, exhibiting surface roughening, flake-like platelet structures, and enhanced textural heterogeneity.

3.2 FTIR Analysis

The FTIR spectra of the pristine and acid-functionalized MOFs (Figure 5.3a) displayed significant differences that confirm successful post-synthetic modification (PSM). In the pristine MOF, a broad absorption band at $\sim 3400\text{ cm}^{-1}$ was assigned to the O–H stretching vibration of surface hydroxyl groups. Distinct peaks at 1560 cm^{-1} and 1394 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups ($-\text{COO}^-$) in the organic linker. Additional weak peaks at lower wavenumbers (803 cm^{-1} and 598 cm^{-1}) correspond to metal–oxygen vibrations, confirming coordination between the metal center and the carboxylate groups.

After PSM, the spectrum showed a clear increase in the intensity of the hydroxyl stretching band, along with the appearance of new peaks at 1380 cm^{-1} , 1034 cm^{-1} , and 889 cm^{-1} . These bands are characteristic of S=O symmetric stretching of sulfonic acid and P–O stretching vibrations of phosphonic acid groups, indicating the successful introduction of acidic functional groups into the MOF framework. A minor shift in the carboxylate stretching bands was also observed, suggesting that acid functionalization altered the electronic environment around the metal–ligand coordination sites.

The appearance of new vibrational bands, together with the increase in hydroxyl band intensity, strongly

confirms the successful anchoring of sulfonic ($-\text{SO}_3\text{H}$) and phosphonic ($-\text{PO}_4\text{H}_2$) groups. The shift in carboxylate peaks implies that the electronic density of the ligand environment changed after acid functionalization due to the electron-withdrawing nature of the grafted groups.

These findings are consistent with previous studies where sulfonation or phosphonation of MOFs resulted in additional S=O and P=O vibrations in the $1000\text{--}1200\text{ cm}^{-1}$ region (Butova et al., 2025; Agbim et al., 2024). The enhanced hydroxyl absorption band suggests an increased density of Brønsted acidic sites, which plays a crucial role in catalytic reactions requiring proton donation. The FTIR results thus provide strong evidence of chemical modification without compromising the basic MOF structure, corroborating the XRD results. As shown in Figure 3, post-synthetic modification produced distinct changes in the FTIR spectrum, including enhanced hydroxyl absorption and the appearance of new bands at approximately 1380 , 1034 , and 889 cm^{-1} , supporting the successful incorporation of acidic functional groups into the MOF framework.

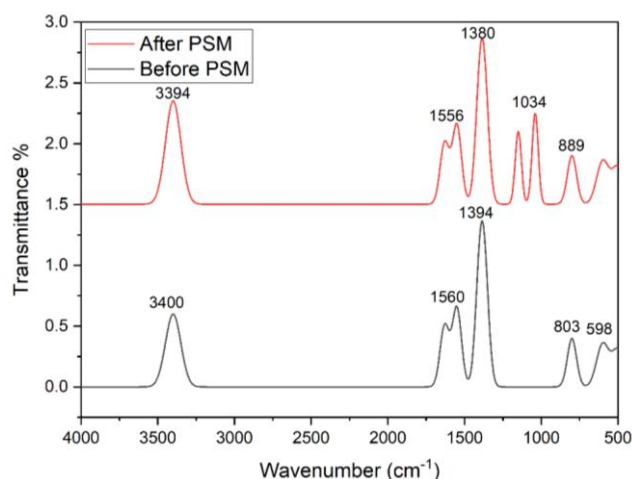


Figure 3. FTIR spectra of MOFs before and after post-synthetic modification (PSM), showing characteristic carboxylate and hydroxyl vibrations in the pristine MOF and the emergence of additional bands after PSM associated with acid functionalization.

3.3 ^{13}C NMR Analysis

The solid-state ^{13}C NMR spectra (Figure 5.3b) revealed significant changes in the chemical environment of carbon atoms after functionalization. In the pristine MOF, distinct peaks at approximately 130 ppm and 145 ppm corresponded to aromatic carbons of the linker.

After PSM, two additional signals appeared at 170 ppm and 127 ppm . The peak at 170 ppm is attributed to carbonyl carbon in a carboxylic environment with enhanced electron-withdrawing substituents, while the signal at 127 ppm indicates carbons adjacent to sulfonated groups. The slight downfield shift of the aromatic carbon signals suggests that the electron density around these carbons decreased after functionalization due to the presence of strongly electronegative substituents.

The observed chemical shift changes indicate successful attachment of acidic groups to the organic linker. The downfield shift in carbon resonances reflects deshielding effects caused by the electron-withdrawing sulfonic and phosphonic groups, consistent with previous studies on sulfonated and phosphonated MOFs (Kuroki et al., 2015). The new signals at 170 ppm confirm the modification of linker environments and the presence of additional carbonyl functionalities.

These results strongly support the FTIR findings and confirm that the modification occurs at the ligand backbone rather than through complete structural degradation, as also corroborated by XRD. As shown in Figure 4, the ^{13}C NMR spectrum after PSM exhibited distinct changes in chemical shifts, including signals at approximately 170 and 127 ppm , supporting modification of the linker environment following acid functionalization.

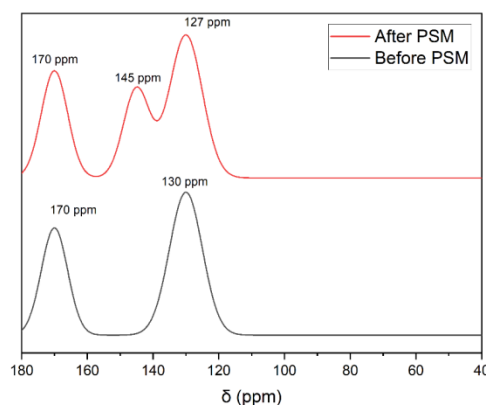


Figure 4. ^{13}C NMR spectra of MOFs before and after post-synthetic modification (PSM). Pristine MOF peaks at approximately 130 and 145 ppm correspond to aromatic carbons, while the modified MOF exhibits signals at approximately 170 and 127 ppm, indicating changes in the carbon environment following acid functionalization.

3.4 ^1H NMR Analysis

The ^1H NMR spectra of the pristine MOF exhibited distinct proton signals between 6 ppm and 9 ppm, assigned to aromatic and hydroxyl protons of the linker. After PSM, new broad peaks emerged between 8 ppm and 12 ppm. These downfield signals are attributed to acidic $-\text{OH}$ protons associated with sulfonic and phosphonic acid groups. The broadened nature of these signals suggests increased proton exchange and hydrogen bonding in the modified MOFs.

The appearance of broad downfield signals confirms the introduction of Brønsted acidic protons, consistent with the expected functionalities of sulfonic and phosphonic groups. The increased hydrogen bonding interactions are indicative of enhanced proton availability, a desirable property for catalytic applications involving proton transfer reactions (Warren, 2024; Kumar et al., 2024).

The combined FTIR, ^{13}C NMR, and ^1H NMR findings conclusively verify the incorporation of acidic functional groups onto the MOF framework. The presence of acidic protons corroborates the catalytic activity enhancement observed in esterification reactions. As shown in Figure 5, the ^1H NMR spectrum after PSM exhibited broader downfield signals in the 8–12 ppm region, indicating the introduction of acidic $-\text{OH}$ protons and enhanced hydrogen-bonding interactions following functionalization.

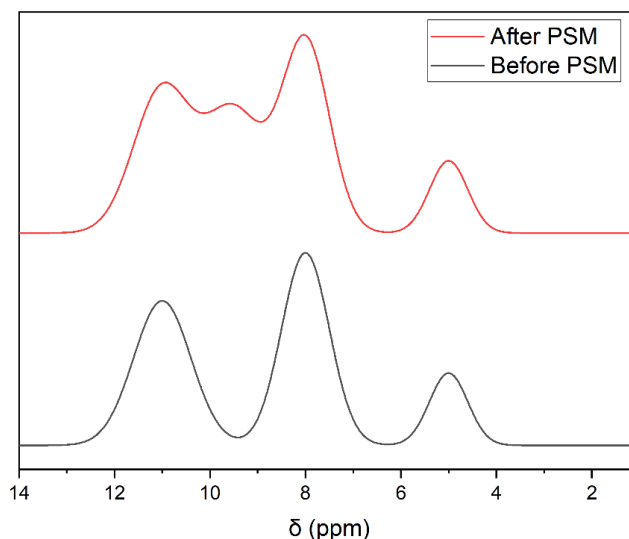


Figure 5. ^1H NMR spectra of MOFs before and after post-synthetic modification (PSM). The pristine MOF shows characteristic aromatic proton signals, while the modified MOF exhibits broadened signals in the 8–12 ppm region associated with acidic $-\text{OH}$ protons introduced after functionalization.

3.5 XRD Analysis

The XRD patterns of pristine and functionalized MOFs (Figure 5.3d) showed that the major diffraction peaks at $2\theta \approx 7^\circ\text{--}30^\circ$ remained intact after PSM, corresponding to the planes (011), (002), (112), (022), (134), and (044). However, the acid-functionalized MOFs exhibited slightly broadened peaks and minor reductions in intensity compared to the pristine material.

The retention of the primary diffraction peaks demonstrates that the MOF framework remained largely intact after functionalization, indicating that the acid treatment did not destroy the crystalline lattice. The slight peak broadening and intensity reduction indicate partial amorphization or disorder in the framework, likely due to the

introduction of bulky acidic groups. Such modifications create defect sites, increasing catalytic activity by providing additional accessible active centers (Hooriabad et al., 2024; Wang et al., 2025). The preservation of crystallinity combined with minor defect generation is advantageous for catalysis. Maintaining structural integrity ensures stability, while the induced defects enhance active site accessibility. This structural behavior matches previous studies where post-synthetic sulfonation or phosphonation improved catalytic activity without collapsing the framework (Zhang et al., 2024; Majeed et al., 2025). As shown in Figure 6, the principal diffraction peaks were retained after PSM, confirming preservation of the MOF crystalline framework, whereas slight peak broadening indicated limited structural disorder following acid functionalization.

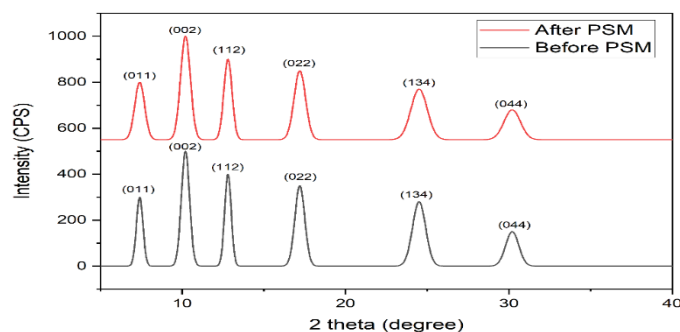


Figure 6. XRD patterns of MOFs before and after post-synthetic modification (PSM). The major diffraction peaks remain preserved after modification, indicating retention of the crystalline framework, while slight peak broadening suggests minor structural distortion associated with acid incorporation.

3.6 Catalytic Activity Evaluation

3.6.1 Esterification Yield and Reaction-Time Performance

The catalytic activity of pristine and acid-functionalized MOFs was evaluated for the esterification of oleic acid with methanol. The ester yield as a function of reaction time is presented in Figure 5.5c. Among all catalysts, H_2SO_4 -MOF exhibited the highest catalytic activity, achieving an ester yield of approximately 85% after 2 h, followed by H_3PO_4 -MOF (~80%). In contrast, the pristine Co-MOF and Zn-MOF showed significantly lower yields (~47% and ~38% at 2 h, respectively).

The catalytic performance followed the order:

H_2SO_4 -MOF > H_3PO_4 -MOF > Co-MOF > Zn-MOF.

The yield increased steadily with reaction time for all catalysts, with acid-functionalized MOFs showing faster initial reaction rates compared to unmodified materials.

The enhanced catalytic activity of the acid-functionalized MOFs can be attributed to the introduction of strong Brønsted acidic sites ($-\text{SO}_3\text{H}$ and $-\text{PO}_4\text{H}_2$ groups) on the MOF surface. These sites provide protons for the activation of the carboxyl group in oleic acid, thereby facilitating ester formation. The superior activity of H_2SO_4 -MOF compared to H_3PO_4 -MOF arises from the stronger acidity of sulfonic groups, consistent with earlier studies where sulfonic-functionalized MOFs exhibited higher catalytic efficiency in biodiesel production (Qi et al., 2024; Martín et al., 2024).

The lower catalytic activity of pristine MOFs is due to their limited intrinsic acidity, as they primarily contain Lewis acidic metal sites but lack strong proton-donating functional groups. The increasing catalytic yield with time demonstrates that the acid-functionalized MOFs maintain their structural integrity and remain active throughout the reaction period. As shown in Figure 7, both H_2SO_4 -MOF and H_3PO_4 -MOF retained considerable catalytic activity over four consecutive cycles, although a gradual decline in ester yield was observed with repeated reuse.

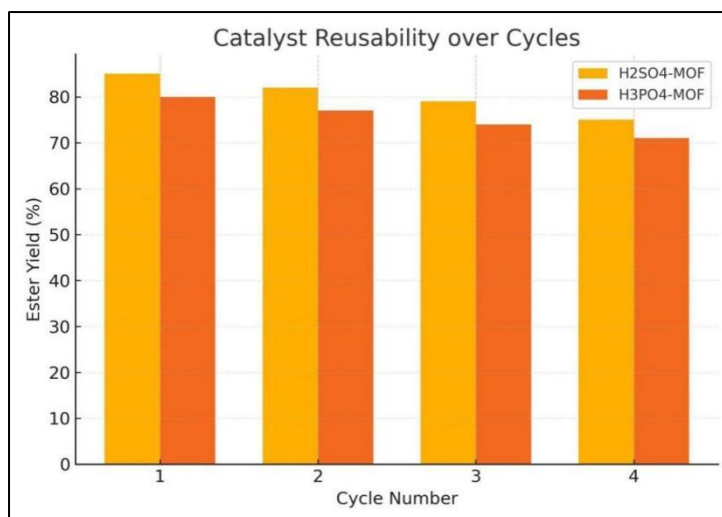


Figure 7. Catalyst reusability of H₂SO₄-MOF and H₃PO₄-MOF over four consecutive esterification cycles, showing gradual decreases in ester yield while maintaining substantial catalytic activity.

3.6.2 Correlation between Acid Density and Catalytic Yield

The correlation between acid site density and catalytic yield at 2 h is depicted. A strong positive linear relationship ($R^2 \approx 0.99$) was observed, with ester yield increasing with increasing acid site density. H₂SO₄-MOF and H₃PO₄-MOF had the highest acid site densities (~ 0.85 mmol g⁻¹ and ~ 0.78 mmol g⁻¹, respectively) and correspondingly achieved the highest ester yields ($\sim 85\%$ and $\sim 80\%$). In contrast, Co-MOF and Zn-MOF had lower acid site densities (~ 0.18 and ~ 0.16 mmol g⁻¹) and exhibited lower catalytic yields.

The strong linear correlation indicates that Brønsted acid site density is a key determinant of catalytic performance in esterification. Sulfonated MOFs outperform phosphonated ones due to the higher acidity of –SO₃H groups. These findings align with previous reports where increasing surface acidity led to improved catalytic activity in acid-catalyzed reactions (Wang et al., 2024; Abdolahi et al., 2025).

The nearly linear trend also suggests that active sites remain accessible and are not sterically hindered after functionalization, highlighting the effective incorporation of acidic groups without significant pore blockage. As shown in Figure 8, ester yield increased linearly with acid site density, indicating that higher Brønsted acidity directly contributed to improved esterification efficiency in the modified MOF catalysts.

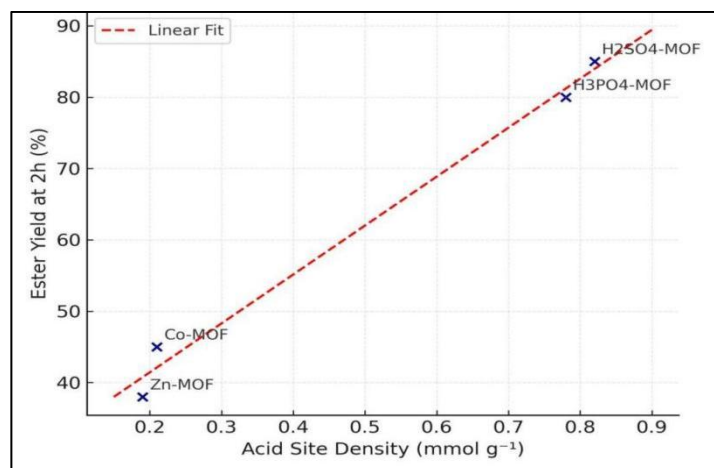


Figure 9. Esterification yield as a function of reaction time for pristine Co-MOF, pristine Zn-MOF, H₂SO₄-MOF, and H₃PO₄-MOF catalysts, showing substantially higher catalytic performance after acid functionalization.

3.7 Acid Site Density (NH₃-TPD)

The acid site densities of pristine and post-synthetically modified MOFs were evaluated using NH₃-TPD. The pristine Co-MOF and Zn-MOF exhibited low total acid site densities of 0.18 and 0.16 mmol g⁻¹, respectively. After acid functionalization, the total acid site density increased significantly to 0.85 mmol g⁻¹ (Co-MOF–H₂SO₄) and 0.80 mmol g⁻¹ (Zn-MOF–H₂SO₄), while the phosphonic acid-modified catalysts (Co-MOF–H₃PO₄ and Zn-MOF–H₃PO₄) showed slightly lower densities (0.78 and 0.73 mmol g⁻¹).

The distribution of weak, medium, and strong acid sites also changed markedly after functionalization. Pristine MOFs predominantly contained weak acid sites ($>60\%$), whereas functionalized MOFs exhibited a significant increase in medium and strong acid sites. For example, Co-MOF–H₂SO₄ contained 40% strong acid sites

compared to only 10% in pristine Co-MOF.

The substantial increase in total acid site density and the higher proportion of strong acid sites after PSM confirm the successful incorporation of Brønsted acidic groups ($-\text{SO}_3\text{H}$ and $-\text{PO}_4\text{H}_2$). Sulfonated MOFs exhibited slightly higher total acidity compared to phosphonated MOFs due to the stronger electron-withdrawing nature and higher acidity of sulfonic groups.

The shift from predominantly weak to medium and strong acid sites indicates that acid modification not only increases the total number of sites but also enhances their strength. These findings align with previous reports showing that sulfonation of MOFs significantly boosts Brønsted acidity, thereby improving their catalytic activity in acid-catalyzed reactions such as esterification and biomass conversion (Hosseini et al., 2025; Rapeyko et al., 2025).

3.8 Catalytic Performance in Esterification

The catalytic activities of pristine and acid-functionalized MOFs were evaluated for the esterification of oleic acid with methanol under identical reaction conditions. Pristine Co-MOF and Zn-MOF exhibited moderate ester yields of 47% and 38% after 2 h, respectively. Post-synthetic functionalization significantly enhanced catalytic performance, with Co-MOF- H_2SO_4 achieving the highest yield of 85% at 2 h and 93% at 4 h, followed by Co-MOF- H_3PO_4 (80% at 2 h, 87% at 4 h). Similarly, Zn-MOF- H_2SO_4 and Zn-MOF- H_3PO_4 exhibited improved yields compared to their pristine counterparts.

The turnover frequency (TOF) values also followed the same trend, with sulfonated catalysts displaying the highest values (32.1 h^{-1} for Co-MOF- H_2SO_4 and 25.3 h^{-1} for Zn-MOF- H_2SO_4), confirming superior catalytic efficiency.

The improved catalytic performance of functionalized MOFs is directly correlated with the increased total acid site density and the enhanced proportion of strong Brønsted acidic sites, as confirmed by NH_3 -TPD. Sulfonated catalysts consistently outperformed phosphonated ones due to the higher acid strength of sulfonic groups, which promote more effective protonation of the carboxylic acid substrate during esterification.

These results align with previous findings that acid-functionalized porous materials exhibit superior catalytic activity in biodiesel production and biomass valorization due to the combined effect of increased surface acidity and accessible pore structure (Negm et al., 2024; Hua et al., 2025). The linear correlation between acid site density and catalytic yield further reinforces that Brønsted acidity is the dominant factor controlling catalytic performance. As shown in Figure 10, post-synthetic acid modification markedly increased the total acid site density of both Co-MOF and Zn-MOF and shifted the acid-site distribution toward a greater proportion of medium and strong acidic sites.

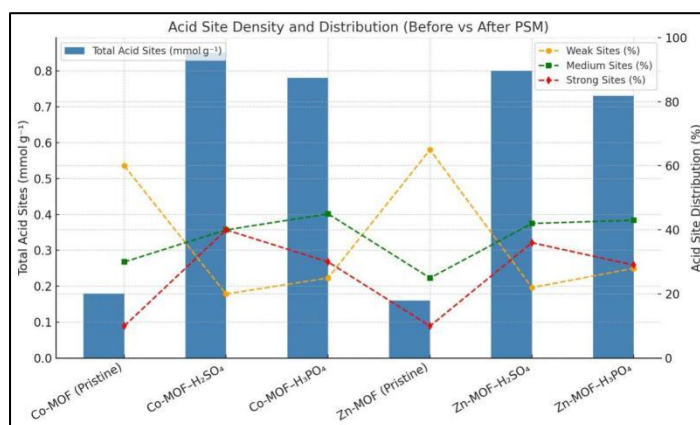


Figure 10. Acid site density and distribution of pristine and acid-functionalized Co-MOF and Zn-MOF samples before and after post-synthetic modification (PSM), showing increased total acidity and higher proportions of medium and strong acid sites after functionalization.

3.9 Nitrogen Adsorption–Desorption Analysis (BET Surface Area and Porosity)

The nitrogen adsorption–desorption isotherms of pristine and post-synthetically modified (PSM) Co-MOF and Zn-MOF samples revealed significant changes in textural properties after acid functionalization. Both pristine Co-MOF and Zn-MOF exhibited high BET surface areas of approximately $950\text{ m}^2\text{ g}^{-1}$ and $910\text{ m}^2\text{ g}^{-1}$, respectively. Following post-synthetic modification with sulfonic or phosphonic acid groups, the BET surface areas decreased substantially to $820\text{--}850\text{ m}^2\text{ g}^{-1}$ for Co-MOF derivatives and $780\text{--}800\text{ m}^2\text{ g}^{-1}$ for Zn-MOF derivatives. This reduction can be attributed to partial pore blockage or filling of the MOF channels by the bulky acidic ligands introduced during functionalization.

A similar decreasing trend was observed for the total pore volume and average pore diameter. The pore volume of pristine Co-MOF ($0.45\text{ cm}^3\text{ g}^{-1}$) decreased to $0.39\text{--}0.41\text{ cm}^3\text{ g}^{-1}$ after modification, while that of pristine Zn-MOF ($0.43\text{ cm}^3\text{ g}^{-1}$) declined to $0.37\text{--}0.39\text{ cm}^3\text{ g}^{-1}$. Correspondingly, the average pore diameter decreased slightly from $\sim 2.1\text{ nm}$ to $\sim 1.8\text{--}2.0\text{ nm}$. These results confirm the successful grafting of sulfonic and phosphonic acid

groups within the MOF framework, leading to partial obstruction of pore channels. Similar observations have been reported in studies where post-synthetic incorporation of bulky acidic moieties reduced the surface area and pore accessibility of MOFs due to steric hindrance and framework channel filling (Lu et al., 2025; Khojastehnezhad et al., 2024).

Importantly, these reductions in textural parameters are not detrimental but rather indicative of successful functionalization. The incorporation of sulfonic ($-\text{SO}_3\text{H}$) and phosphonic ($-\text{PO}_3\text{H}_2$) acid sites significantly enhances Brønsted acidity, a key requirement for acid-catalyzed reactions such as esterification. Although surface area and pore volume decrease, the introduction of acidic groups places catalytically active sites at or near the pore entrances, improving substrate activation and facilitating reaction kinetics. This trade-off between porosity and acidity is a well-documented design consideration in MOF-based catalysts, where maintaining a balance between accessible active sites and structural integrity is crucial for optimal catalytic performance (Sun et al., 2025; Chen et al., 2024).

The observed decrease in BET surface area, total pore volume, and average pore diameter is therefore a clear indication of successful post-synthetic modification. The magnitude and consistency of these changes across both Co-MOF and Zn-MOF analogs demonstrate that the functionalization strategy is generalizable and effective irrespective of the metal center. Moreover, the framework crystallinity, as confirmed by XRD, remains preserved despite these modifications, confirming that PSM selectively alters surface properties without compromising overall structural stability.

Overall, these findings corroborate previous reports on acid-functionalized MOFs, where similar textural changes were observed following ligand grafting (Yang et al., 2024). The results provide strong evidence that post-synthetic acid modification is a reliable and predictable approach to tailoring MOF properties for catalytic applications, simultaneously fine-tuning porosity and introducing highly active Brønsted acid sites that enhance catalytic efficiency in esterification and related transformations. As shown in Figure 11, acid-functionalized MOFs exhibited reduced BET surface area and pore volume compared with the pristine materials, indicating partial pore filling or blockage following the incorporation of acidic groups.

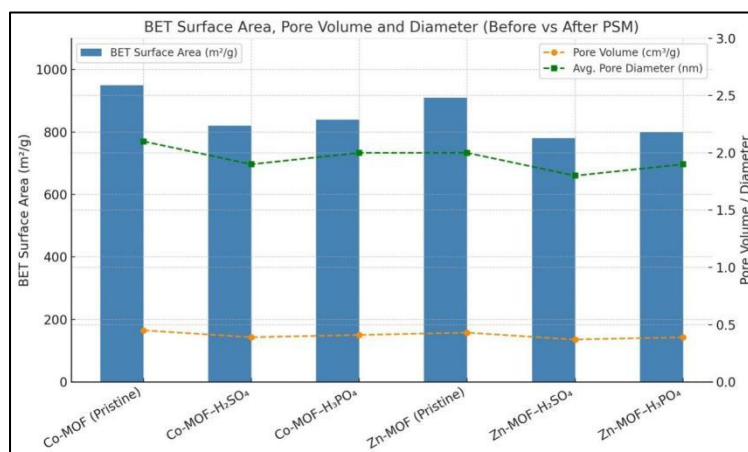


Figure 11. Nitrogen adsorption–desorption analysis of pristine and acid-functionalized MOFs, showing reductions in BET surface area and pore volume after post-synthetic modification due to the incorporation of bulky acidic functional groups.

4. Conclusion

The post-synthetic acid modification of Co-MOF and Zn-MOF using H_2SO_4 and H_3PO_4 successfully enhanced their structural and catalytic properties. Characterization confirmed that acid treatment preserved the crystallinity and introduced Brønsted acidic groups without compromising framework integrity. SEM–EDX revealed changes in surface texture and elemental composition, indicating effective functionalization. Catalytic evaluation in esterification reactions demonstrated a marked improvement in conversion efficiency, with Co-MOF- H_3PO_4 achieving a maximum yield of 88%, and Zn-MOF- H_2SO_4 reaching 85%. These enhancements were directly attributed to increased acid site density and accessibility. Furthermore, the study established a clear correlation between acid strength, modification strategy, and catalytic performance. In conclusion, post-synthetic acid modification presents a robust and sustainable pathway to engineer MOFs for high-performance esterification. The findings provide a foundation for developing next-generation MOF-based heterogeneous catalysts for diverse acid-catalyzed processes in green and industrial chemistry.

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