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Palladium-containing magnetic UiO-66–NH₂ as a highly powerful and recoverable nanocatalyst for the reduction of nitrobenzenes

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Magnetically recoverable porous materials with tunable surface chemistry are of growing interest for heterogeneous catalysis due to their ease of separation, structural versatility, and high surface accessibility. However, integrating multiple functional components into a single stable and reusable catalytic platform remains a significant challenge. In this study, the design and synthesis of a hierarchical nanocomposite, Fe₃O₄@MCM-41@UiO-66/SB–Pd, through a stepwise functionalization approach are reported. The strategy integrates a magnetic Fe₃O₄ core, mesoporous silica, a microporous UiO-66–NH₂ framework, and a Schiff base-coordinated Pd complex to yield a structurally ordered and catalytically active nanocomposite. The resulting nanomaterial exhibited a high surface area (249.1 m² g^{−1}), hierarchical porosity, thermal stability, and superparamagnetic behavior. Comprehensive characterization confirmed the successful incorporation of all functional groups while maintaining crystallinity. The Fe₃O₄@MCM-41@UiO-66/SB–Pd nanocomposite demonstrated high catalytic efficiency for the reduction of nitroarenes under mild conditions, along with excellent reusability. These results highlight a promising approach for designing hybrid catalytic materials with hierarchical porosity, enhanced stability, and practical recyclability for environmentally relevant transformations.

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1. Introduction

Nowadays, the design and development of multifunctional materials with tailored properties for diverse applications have become a major research focus in the field of materials science. In this regard, metal–organic frameworks (MOFs) have garnered significant attention over the past few decades, owing not only to their high surface areas and porosities, but also to their highly tunable pore structures and functionalities.^{1–7} By carefully selecting appropriate metal ions or clusters and organic linkers, a wide variety of MOFs have been synthesized. Furthermore, the properties of MOFs can be further fine-tuned through post-synthetic modification (PSM), offering enhanced versatility. These distinctive features have positioned MOFs as promising candidates for a wide range of applications, including gas storage, drug delivery, biosensors, and catalysis.^{8–16} However, many MOFs have been shown to be unstable when exposed to moisture. This instability is mainly due to the presence of metal–ligand coordination bonds, which make them more susceptible to hydrolysis compared to their inorganic counterparts, such as zeolites.^{17,18} More recently, composites combining MOFs with mesoporous silica have gained increasing attention due to their hierarchical micro- and mesoporous structures.^{19–22} To fabricate such composites, SBA-

15 and MCM-41 featuring highly ordered channels, tunable pore sizes, and excellent thermal stability are commonly used as matrices.^{23–25} The incorporation of mesoporous silica introduces additional mesopores into the composites, which facilitates diffusion and mass transfer. Moreover, the hydrothermal stability and mechanical strength of MOFs can also be significantly enhanced.^{26,27} Some of the recently developed composites in this regard are MOF-5@SBA-15,²⁶ HKUST-1@SBA-15,²⁷ silica@CAT/ZIF-8,²⁸ Zr–MOF-808/MCM-41,²⁴ PMO₁₂@MOF-808@SBA-15,²⁹ Cu/SiO₂–MOF,³⁰ and ZnGlu/MOF/SBA-16.³¹ However, some of the aforementioned catalytic systems suffer from catalyst leaching, separation difficulties, and poor recoverability, which limit their practical applications. Therefore, the design of integrated nanocatalysts (INCs) based on MOFs with multiple components and a hierarchically complex structure has recently attracted significant research attention, from both fundamental and industrial perspectives.

On the other hand, aromatic amines play a crucial role in the herbicide, dye, agrochemical, and pesticide industries. Furthermore, they serve as key intermediates for the synthesis of various compounds, including diazonium salts, isocyanates, azo compounds, and amides.^{32–34} Sodium borohydride (NaBH₄) has been proposed as a promising fuel source for supplying hydride ions to reduce nitrobenzenes to their corresponding amines under mild conditions. However, NaBH₄ exhibits limited reducing capability in the absence of suitable additives.^{35–38} Therefore, this reagent is typically employed in

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the presence of metallic catalysts. Another widely used and conventional approach for synthesizing aromatic amines involves the catalytic hydrogenation of the corresponding nitroarenes.^{39,40} However, the homogeneous protocols for reduction of nitroarenes have different disadvantages such as separation of the catalyst and product. Therefore, it is still necessary to design effective and recoverable catalytic systems resolving these issues. A promising approach to address these limitations involves the integration of magnetic nanoparticles such as Fe₃O₄ as catalyst supports, owing to their high surface area, chemical stability, and excellent magnetic responsiveness, which enable efficient separation and reuse in heterogeneous catalytic processes.^{41–44}

In view of the above, the present study aims to develop a magnetically recoverable, hierarchically porous nanocatalyst combining an Fe₃O₄ magnetic core, mesoporous MCM-41 silica, and microporous UiO-66–NH₂ MOF functionalized with a Schiff base–Pd complex. This multicomponent design addresses common challenges in catalytic systems such as catalyst separation, metal leaching, and recyclability, thereby offering a sustainable and efficient platform for the reduction of nitroarenes under mild and green conditions.

2. Experimental

2.1. Synthesis of Fe₃O₄@MCM-41

Fe₃O₄ and Fe₃O₄@SiO₂ nanoparticles were initially synthesized according to our previously reported procedures.^{45,46} Subsequently, 0.6 g of Fe₃O₄@SiO₂ nanoparticles were ultrasonically dispersed in a mixture of deionized water (60 mL) and ethanol (50 mL) for 20 min. Then, 3 mL of 25% ammonia solution and 1 g of cetyltrimethylammonium bromide (CTAB) were added under continuous stirring at room temperature (RT) for 30 min. Thereafter, 0.7 mL of tetramethyl orthosilicate (TMOS) was added dropwise, and the mixture was stirred at RT for an additional 2 h. The resulting material was then statically heated under an argon atmosphere at 100 °C for 72 h. The obtained precipitate was collected using a magnet, washed with deionized water and ethanol, and dried at 65 °C for 7 h. Finally, the CTAB template was removed by calcination at 500 °C for 6 h. The final product was denoted as Fe₃O₄@MCM-41.

2.2. Synthesis of Fe₃O₄@MCM-41@UiO-66–NH₂

Initially, 1.0 g of Fe₃O₄@MCM-41 magnetic nanoparticles was fully dispersed in 50 mL of DMF under ultrasonic irradiation for 30 min. Subsequently, 0.433 g of zirconium tetrachloride, dissolved in 20 mL of DMF, was added to the reaction vessel and dispersed under ultrasonic conditions. After 20 min, 0.362 g of 2-aminoterephthalic acid (ATA), dissolved in 20 mL of DMF, was introduced into the vessel, and the reaction mixture was ultrasonicated for an additional 15 min to ensure complete dispersion. The resulting mixture was then transferred into an autoclave and heated at 120 °C for 24 h under static conditions. The synthesized material was collected using a magnet and washed several times with DMF (three times) and acetone (four

times). Finally, the obtained solid was dried at 70 °C and denoted as Fe₃O₄@MCM-41@UiO-66–NH₂.

2.3. Synthesis of Fe₃O₄@MCM-41@UiO-66/SB

To achieve this, the Fe₃O₄@MCM-41@UiO-66–NH₂ nanocomposite (0.5 g) was dispersed in 30 mL of dry toluene at 25 °C for 30 min. Then, salicylaldehyde (2 mL) was added to the reaction vessel and it was allowed to reflux for 24 h. Following centrifugation, the resultant material was washed with dry EtOH and allowed to dry for 7 h at 70 °C. The solid product was denoted as Fe₃O₄@MCM-41@UiO-66/SB.

2.4. Synthesis of Fe₃O₄@MCM-41@UiO-66/SB–Pd

For this, 0.5 g of Fe₃O₄@MCM-41@UiO-66/SB was fully dispersed in 20 mL of dry EtOH at 25 °C for 30 min. Then, 1 mmol of Pd(OAc)₂ was added and the reaction vessel was agitated at RT for 24 h. Following centrifugation, the final product was washed with dry EtOH, dried at 70 °C for 6 h and denoted as Fe₃O₄@MCM-41@UiO-66/SB–Pd.

2.5. Procedure for the reduction of nitrobenzenes using Fe₃O₄@MCM-41@UiO-66/SB–Pd

For this purpose, 1 mmol of nitrobenzene, 2 mmol of NaBH₄, and 0.01 g of the Fe₃O₄@MCM-41@UiO-66/SB–Pd catalyst were added to a reaction vessel containing 10 mL of distilled water. The resulting mixture was stirred at RT and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated using a magnet. The aqueous-soluble impurities were effectively removed by decantation using a biphasic solvent system consisting of water and ethyl acetate. The resulting crude products were purified either by evaporation of the organic phase or by recrystallization from ethanol.

2.6. FT-IR and NMR data of aniline products

2.6.1. 4-Hydroxyaniline (2a). IR (KBr, cm^{−1}): 3656 (NH, stretching vibration), 3509 (OH, stretching vibration), 3046 (=C–H, stretching vibration sp²), 1505, 1622 (C=C, Ar stretching sp²).

2.6.2. 4-Methoxyaniline (2b). IR (KBr, cm^{−1}): 3425, 3348 (NH, stretching vibration), 3021 (=C–H, stretching vibration sp²), 2880 (C–H, stretching vibration sp³), 1632, 1432 (C=C, Ar stretching sp²), 1210 (C–O, stretching vibration).

2.6.3. Benzene-1,2-diamine (2c). IR (KBr, cm^{−1}): 3583, 3453 (NH, stretching vibration), 3031 (=C–H, stretching vibration sp²), 1516, 1617 (C=C, Ar stretching sp²).

2.6.4. 2-Aminobenzyl alcohol (2d). IR (KBr, cm^{−1}): 3393, (NH, stretching vibration), 3142 (OH, stretching vibration), 2991 (C–H, stretching vibration sp³), 1453, 1613 (C=C, Ar stretching sp²).

2.6.5. 4-Bromoaniline (2e). IR (KBr, cm^{−1}): 3481, 3408 (NH, stretching vibration), 3040 (=C–H, stretching vibration sp²), 1498, 1622 (C=C, Ar stretching sp²). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 5.29 (s, NH₂, 2H), 6.52 (d, *J* = 8.8, 2H), 7.14 (d, *J* = 8.8, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 106.5, 116.2, 131.8, 148.51.



2.6.6. 4-Chloroaniline (2f). IR (KBr, cm^{-1}): 3478, 3412 (NH, stretching vibration), 3026 (=C-H, stretching vibration sp^2), 1519, 1625 (C=C, Ar stretching sp^2). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ (ppm) 4.6 (s, NH_2 , 2H), 6.67 (d, $J = 8.5$, 2H), 6.72 (d, $J = 8.5$, 2H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ (ppm) 114.9, 115.5, 142.7, 151.2.

3. Results and discussion

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB-Pd}$

Scheme 1 depicts the synthesis procedure of $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB-Pd}$. Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs were first prepared according to previous methods.⁴⁷ Mesoporous silica-coated magnetic ($\text{Fe}_3\text{O}_4@\text{MCM-41}$) NPs were then prepared *via* the surfactant-directed condensation of TMOS over $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs under basic conditions. Next, $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66-\text{NH}_2$ was solvothermally synthesized *via* chemical attachment of ZrCl_4/ATA based MOF on $\text{Fe}_3\text{O}_4@\text{MCM-41}$.

$\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66-\text{NH}_2$ was then chemically reacted with salicylaldehyde to afford $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB}$. The $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB-Pd}$ nanocatalyst was finally obtained by treating the $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB}$ support with $\text{Pd}(\text{OAc})_2$.

The successful synthesis of the $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB-Pd}$ composite was confirmed by FT-IR spectroscopy (Fig. 1). The peaks at 580 and 3409 cm^{-1} are attributed to the Fe-O and OH stretching vibrations, respectively (Fig. 1a and b).⁴⁸ Upon coating with MCM-41 silica, the additional bands at 1100 and 800 cm^{-1} , corresponding to Si-O-Si asymmetric and symmetric stretching vibrations, respectively, indicate the successful formation of MCM-41 on magnetite NPs (Fig. 1b).⁴⁹ For UiO-66- NH_2 , the absorption bands at 3460 and 3351 cm^{-1} correspond to asymmetric and symmetric N-H stretching vibrations, respectively, while the band at 1660 cm^{-1} is assigned to the C=O stretching vibration of carboxylate groups. The characteristic asymmetric and symmetric stretching vibrations of



Scheme 1 Preparation of $\text{Fe}_3\text{O}_4@\text{MCM-41}@UiO-66/\text{SB-Pd}$.





Fig. 1 FT-IR spectra of (a) Fe₃O₄, (b) Fe₃O₄@MCM-41, (c) UiO-66-NH₂, and (d) Fe₃O₄@MCM-41@UiO-66/SB-Pd.

coordinated carboxylate groups appear at 1574 and 1388 cm⁻¹, respectively. Additionally, the aromatic C=C stretching band is observed at 1495 cm⁻¹. The Zr-O stretching vibrations are also evidenced by the bands at 661 and 768 cm⁻¹ (Fig. 1c).⁵⁰⁻⁵² In the final Fe₃O₄@MCM-41@UiO-66/SB-Pd composite, the retention of all characteristic bands from the core-shell structure indicates structural integrity. Notably, a new absorption band appears at 1650 cm⁻¹, which is attributed to the C=N stretching vibration of the Schiff base linkage. Additionally, the disappearance of N-H stretching bands (at 3460 and 3351 cm⁻¹) confirms the successful condensation between amine and aldehyde groups to form the imine bond (Fig. 1d).⁵³ These results confirm the successful construction of the designed composite.

The wide-angle powder X-ray diffraction (WAPXRD) analysis was employed to investigate the crystalline structure of the synthesized nanomaterials (Fig. 2). As illustrated, the WAPXRD pattern of Fe₃O₄@MCM-41 exhibits diffraction peaks at 2θ ≈ 30.3°, 35.6°, 43.2°, 53.5°, 57.1°, and 62.7°, which correspond to the (220), (311), (400), (422), (511), and (440) crystal planes of the Fe₃O₄ NPs (Fig. 2a).⁵⁴ These peaks are in good agreement with the standard JCPDS card No. 19-0629, confirming the cubic



Fig. 2 WAPXRD patterns of (a) Fe₃O₄@MCM-41, (b) UiO-66-NH₂, and (c) Fe₃O₄@MCM-41@UiO-66/SB-Pd.

spinel structure of magnetite.^{55,56} For UiO-66-NH₂, multiple sharp diffraction peaks observed at 2θ values of 8.6°, 14.8°, 17.3°, 22.2°, 25.9°, 30.7°, 32.1°, 35.5°, 37.7°, 40.5°, 43.3°, 50.2°, and 56.9° correspond to the crystal lattice exhibiting *Fm3m* symmetry of zirconium benzene carboxylate units. This indicates a highly crystalline framework of UiO-66-NH₂ (Fig. 2b).⁵⁷ The WAPXRD pattern of the final nanocomposite, Fe₃O₄@MCM-41@UiO-66/SB-Pd (Fig. 2c), displays the characteristic



Fig. 3 Low-angle PXRD pattern of Fe₃O₄@MCM-41@UiO-66/SB-Pd.





Fig. 4 EDX spectrum of $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$.

diffraction peaks of both Fe_3O_4 and UiO-66-NH_2 , confirming the successful synthesis of the hybrid material. Moreover, the observed reduction in peak intensity in the final nanocomposite can be attributed to the incorporation of UiO-66-NH_2 into the magnetic MCM-41 framework.

The low-angle PXRD pattern of $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$ displays a distinct diffraction peak at $2\theta \approx 2.2^\circ$ (Fig. 3), corresponding to the (100) reflection of the ordered hexagonal mesophase of MCM-41. This result confirms that the mesoporous structure of MCM-41 is well preserved after the successive functionalization and MOF incorporation steps.

The energy-dispersive X-ray (EDX) analysis was also carried out to investigate the existence of expected elements. As

depicted, the signals of Fe, O, Si, C, N, Zr, and Pd prove successful synthesis of the designed material (Fig. 4).

Moreover, the EDX-mapping analysis clearly demonstrated the uniform distribution of the aforementioned elements in the $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$ framework (Fig. 5).

Thermal stability and composition of $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$ were examined using TG analysis. As presented in Fig. 6, the TG curve demonstrates four weight loss steps. The first stage below 150°C is caused by the removal of physically adsorbed water, indicating a moisture content of about 5% in the sample. The second weight loss ($\sim 10\%$) between 170 and 230°C corresponds to the thermal decomposition of the remaining CTAB surfactant. A significant weight



Fig. 5 EDX-mapping of $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$.



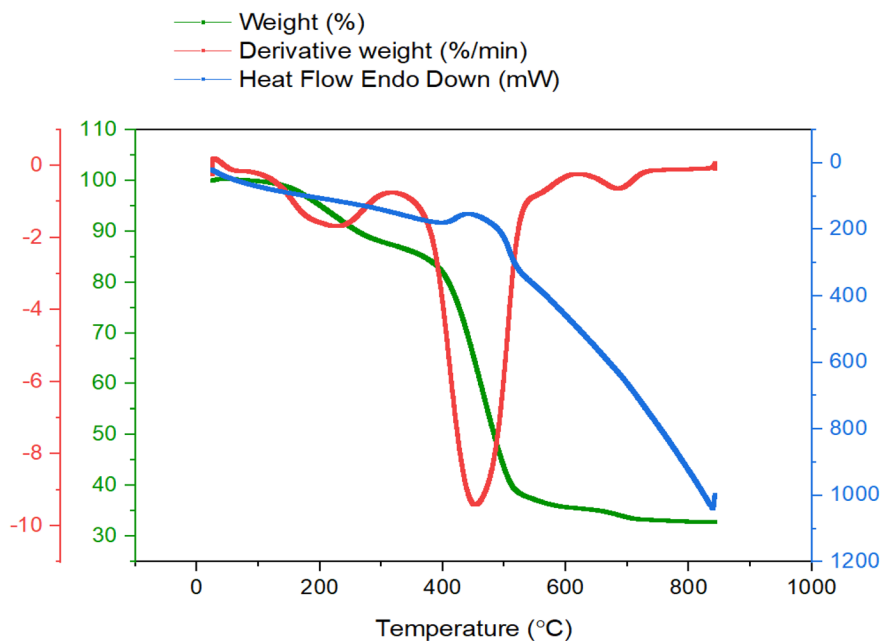


Fig. 6 TG curve of $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$.

loss ($\sim 50\%$) occurs between 235 and 700 °C due to degradation of Schiff-base moieties and organic ligands of the UiO-66 framework and also combustion of residual carbon.^{58,59} These findings confirm the thermal robustness of the designed composite.

The morphology of $\text{Fe}_3\text{O}_4@MCM-41$, UiO-66- NH_2 and $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$ was studied using SEM, as shown in Fig. 6. Analysis of the images revealed that $\text{Fe}_3\text{O}_4@MCM-41$ NPs have good spherical morphology with uniform particle size (Fig. 7a). This also showed that UiO-66- NH_2 crystallized in



Fig. 7 SEM images of (a) $\text{Fe}_3\text{O}_4@MCM-41$, (b) UiO-66- NH_2 , and (c) $\text{Fe}_3\text{O}_4@MCM-41@UiO-66/SB-Pd$.





Fig. 8 N_2 adsorption-desorption isotherms of $Fe_3O_4@MCM-41@UiO-66/SB-Pd$.

well-defined octahedral structures with smooth surfaces and uniform size distribution (Fig. 7b). Upon formation of the final composite, $Fe_3O_4@MCM-41@UiO-66/SB-Pd$ (Fig. 7c), a noticeable change in morphology is observed. The particles become

more irregular with a complex surface topology resulting from surface functionalization, confirming the effective immobilization of $UiO-66-NH_2$ within the magnetic $MCM-41$ nanocomposite.

The specific surface area and porosity of $Fe_3O_4@MCM-41@UiO-66/SB-Pd$ were investigated using nitrogen adsorption-desorption measurements at 77 K. As shown in Fig. 8, the isotherm displays a typical type IV profile with an H1-type hysteresis loop, which is characteristic of mesoporous materials and can be attributed to the presence of $MCM-41$. Additionally, the sharp uptake at low relative pressures indicates the existence of micropores, likely originating from the $UiO-66-NH_2$ framework. The composite exhibits a high specific surface area of $249.1 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of 1.2 nm. This combination of micro- and mesoporosity, along with the large surface area, renders the material highly suitable for catalytic and adsorption applications.

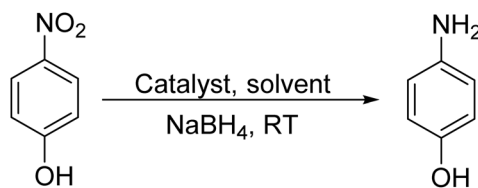
The magnetic properties of materials were investigated using a vibrating sample magnetometer (VSM) (Fig. 9). The saturated magnetization values of $Fe_3O_4@SiO_2$ (Fig. 9a), $Fe_3O_4@MCM-41$ (Fig. 9b) and $Fe_3O_4@MCM-41@UiO-66/SB-Pd$ (Fig. 9c) were found to be 56, 40 and 20 emu g^{-1} , respectively. This gradual reduction in magnetic saturation is attributed to the well coating of the $MCM-41$ shell and $UiO-66-NH_2$ around Fe_3O_4 NPs.



Fig. 9 VSM curves of (a) $Fe_3O_4@SiO_2$, (b) $Fe_3O_4@MCM-41$ and (c) $Fe_3O_4@MCM-41@UiO-66/SB-Pd$.



Table 1 Effect of catalyst loading and solvent on the reduction of 4-nitrophenol



| Entry | Catalyst | Catalyst amount (g) | Solvent | Time (min) | Yield ^a (%) |
|----------------|---|---------------------|------------------|------------|------------------------|
| 1 | — | — | H ₂ O | 60 | — |
| 2 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.005 | H ₂ O | 30 | 81 |
| 3 ^b | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.01 | H ₂ O | 30 | 95 |
| 4 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.015 | H ₂ O | 30 | 96 |
| 5 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.01 | MeOH | 30 | 78 |
| 6 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.01 | EtOH | 30 | 59 |
| 7 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.01 | THF | 30 | 43 |
| 8 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | 0.01 | DMF | 30 | 31 |
| 9 | Fe ₃ O ₄ @MCM-41@UiO-66/SB | 0.01 | H ₂ O | 30 | — |
| 10 | Fe ₃ O ₄ @MCM-41@UiO-66-NH ₂ | 0.01 | H ₂ O | 30 | — |
| 11 | Fe ₃ O ₄ @MCM-41 | 0.01 | H ₂ O | 30 | — |

^a Isolated yield. ^b Optimized conditions.

3.2. Catalytic performance

After the comprehensive characterization of Fe₃O₄@MCM-41@UiO-66/SB-Pd, its performance was studied in the reduction of nitroarenes in the presence of NaBH₄ at room temperature (RT). The effect of different parameters was studied in the reduction of 4-nitrophenol as a reaction model (Table 1). As shown, in the absence of the catalyst, along with 2 mmol of NaBH₄, no reduction was observed (Table 1, entry 1). To determine the optimal amount of the catalyst, a model reaction was carried out using different catalyst loadings (Table 1, entries 2–4). The results indicated that the highest yield is obtained in the presence of 0.01 g of Fe₃O₄@MCM-41@UiO-66/SB-Pd. Notably, increasing the catalyst loading beyond this amount did not result in a significant improvement in reaction progress (Table 1, entry 3 vs. entry 4). Subsequently, to investigate the effect of

the solvent, the model reaction was conducted in various solvents including H₂O, EtOH, MeOH, THF, and DMF. The results revealed that the reaction proceeded more efficiently in polar protic solvents, and H₂O was selected as a green solvent (Table 1, entry 3 vs. entries 5–8). In another experiment, the role of palladium species was evaluated by conducting the model reaction in the presence of Pd-free Fe₃O₄@MCM-41, Fe₃O₄@MCM-41@UiO-66-NH₂, and Fe₃O₄@MCM-41@UiO-66/SB nanocomposites. The obtained results revealed that no product is formed in the absence of palladium, indicating the key role of Pd species as active catalytic centers (Table 1, entry 3 vs. entries 9–11). Therefore, the optimal reaction conditions for the reduction of nitrobenzenes were identified as using 0.01 g of Fe₃O₄@MCM-41@UiO-66/SB-Pd in water at RT (Table 1, entry 3).

Table 2 Reduction of nitrobenzenes using Fe₃O₄@MCM-41@UiO-66/SB-Pd

| Entry | R | Time (min) | Product | Yield (%) | M.P. (°C) | Reported M.P. (°C) (ref.) |
|-------|----------------------|------------|---------|-----------|-----------|---------------------------|
| 1 | 4-OH | 30 | 2a | 95 | 184–186 | 185–186 (ref. 60) |
| 2 | 4-MeO | 27 | 2b | 90 | 57–59 | 59–61 (ref. 60) |
| 3 | 2-NH ₂ | 27 | 2c | 88 | 104–106 | 106–108 (ref. 60) |
| 4 | 2-CH ₂ OH | 30 | 2d | 86 | 80–82 | 80–82 (ref. 60) |
| 5 | 4-Br | 25 | 2e | 93 | 63–65 | 60–63 (ref. 60) |
| 6 | 4-Cl | 23 | 2f | 96 | 68–70 | 70–72 (ref. 46) |



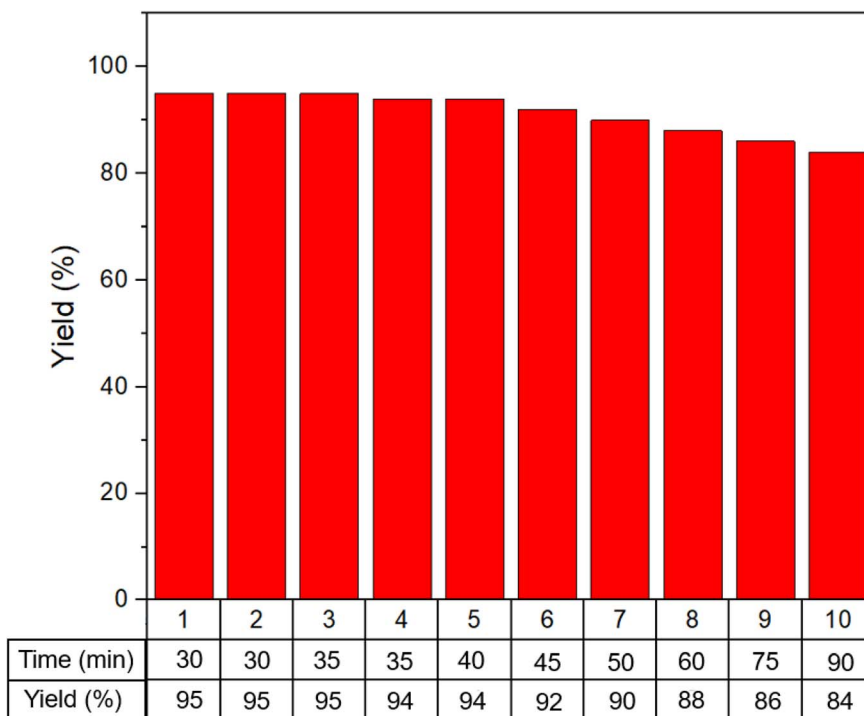


Fig. 10 Recoverability and reusability of $\text{Fe}_3\text{O}_4@\text{MCM}-41@\text{UiO}-66/\text{SB}-\text{Pd}$.

After optimizing the reaction conditions, a wide range of nitroaromatic derivatives were examined in the reduction reaction (Table 2). The results revealed that all nitroaromatic compounds bearing either electron-withdrawing or electron-donating substituents are efficiently converted into the

corresponding amines in excellent yields using the $\text{Fe}_3\text{O}_4@\text{MCM}-41@\text{UiO}-66/\text{SB}-\text{Pd}$ catalyst. These findings highlight the high catalytic activity and selectivity of the designed nano-composite in this process.



Fig. 11 FTIR spectra of (a) fresh and (b) recovered $\text{Fe}_3\text{O}_4@\text{MCM}-41@\text{UiO}-66/\text{SB}-\text{Pd}$ catalyst.



Table 3 Comparative study of the efficiency of Fe₃O₄@MCM-41@UiO-66/SB-Pd with that of former catalysts in the reduction of nitrobenzenes

| Entry | Catalyst | Reaction conditions | Recovery times | Ref. |
|-------|---|--|----------------|-----------|
| 1 | Pd@A-ZIF-67 | H ₂ O : EtOH (1 : 1), NaBH ₄ , RT, catalyst (0.05 mol%) | 6 | 61 |
| 2 | SiO ₂ @β-CD@Pd-PDR | H ₂ O, NaBH ₄ , RT, catalyst (20 mg) | 10 | 62 |
| 3 | Pd@CQD@Fe ₃ O ₄ | H ₂ O : EtOH (5 : 1), NaBH ₄ , RT, catalyst (0.008 mol%) | 7 | 63 |
| 4 | Co@NC | H ₂ O, NaBH ₄ , RT, catalyst (8 mg) | 6 | 64 |
| 5 | Fe ₃ O ₄ /PVA-10% Ag | EtOH, N ₂ H ₄ ·H ₂ O, 70 °C, catalyst (30 mg) | 5 | 65 |
| 6 | Pd-NHC-γ-Fe ₂ O ₃ - <i>n</i> -butyl-SO ₃ H | H ₂ O, NaBH ₄ , RT, catalyst (0.6 mol%) | 6 | 66 |
| 7 | Fe ₃ O ₄ @MCM-41@UiO-66/SB-Pd | H ₂ O, NaBH ₄ , RT, catalyst (0.01 g) | 9 | This work |

Considering the importance of the stability of the catalyst for its practical applications, in the next study, the recyclability of the Fe₃O₄@MCM-41@UiO-66/SB-Pd catalyst was evaluated in the model reaction. For this, upon reaction completion, the catalyst was efficiently recovered using an external magnet, thoroughly washed with EtOH, and dried prior to reuse in subsequent cycles. As illustrated in Fig. 10, the catalyst retained its catalytic activity over nine consecutive runs with negligible loss in performance. These findings confirm the effective immobilization and high stability of Pd species on the support throughout the reaction cycles.

The structural stability of the Fe₃O₄@MCM-41@UiO-66/SB-Pd catalyst after recycling was evaluated using FT-IR spectroscopy. As shown in Fig. 11, the FT-IR spectra of the fresh and reused catalyst after the nine reaction cycles have the same pattern with no noticeable change in the characteristic absorption bands. This observation confirms that the catalyst retained its structural integrity upon repeated use, highlighting its excellent chemical stability and reusability.

Furthermore, the stability and heterogeneous nature of the Fe₃O₄@MCM-41@UiO-66/SB-Pd catalyst were evaluated through a leaching test. In this procedure, the catalyst was magnetically separated from the reaction mixture upon reaching approximately 50% conversion. The resulting residue was then stirred under identical reaction conditions for an additional 60 min. Interestingly, no appreciable increase in product formation was observed, indicating the absence of active Pd species in the solution and confirming the truly heterogeneous character of the catalyst.

In the next study, the performance of Fe₃O₄@MCM-41@UiO-66/SB-Pd was compared to that of other previously reported catalytic systems used in the reduction of nitroarene reaction (Table 3). The results revealed that the present catalyst provides significant advantages regarding reaction temperature, catalyst loading, and recyclability. These outcomes highlight the high efficiency, stability, and durability of the designed catalyst.

4. Conclusion

In summary, a multifunctional composite, Fe₃O₄@MCM-41@UiO-66/SB-Pd, was successfully fabricated through a step-wise surface functionalization strategy. MCM-41 served as a structural bridge, enabling uniform integration of UiO-66-NH₂ nanocrystals and Schiff base-Pd complexes while maintaining magnetic properties of Fe₃O₄ NPs. The resulting catalyst

combined the high surface area and accessible pore architecture of both mesoporous and microporous components with the catalytic functionality of Pd active sites. Comprehensive physicochemical characterization confirmed the retention of crystallinity, hierarchical porosity, thermal stability, and superparamagnetic behavior throughout the synthesis. Owing to these features, the composite demonstrated efficient catalytic performance in the reduction of nitroarenes under mild conditions, along with excellent magnetic recoverability and reusability. Importantly, the high reusability of the catalyst combined with simple magnetic separation reduces the overall operational cost, making it a cost effective alternative to conventional homogeneous and heterogeneous catalytic systems. These findings demonstrate the potential of such hybrid composites for environmentally benign catalytic applications and offer a promising platform for future multifunctional material design.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: raw data of performed analyses. See DOI: <https://doi.org/10.1039/d5na00543d>.

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