

Role of Lewis Acid Metal Centers in Metal–Organic Frameworks for Ultrafast Reduction of 4-Nitrophenol

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Abstract: Metal–Organic Frameworks (MOFs) can be a good alternative to conventional catalysts because they are non-toxic and can be selective without compromising efficiency. Nano MOFs such as UiO-66 have proven themselves to be competitive in the catalytic family. In this study, we report the excellent catalytic behavior of UiO-66 MOF in the reduction of a model reaction: 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) over MOF-5 (Zn-BDC) and MIL-101 (Fe-BDC). Nano UiO-66 crystals were synthesized by a hydrothermal process and characterized by Powder X-ray Diffraction, Diffused Reflectance UV-Vis spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy. The catalysts' performance during the hydrogenation reduction reaction from 4-NP to 4-AP was investigated in the presence of a reducer, NaBH₄. The UiO-66 nano crystals exhibited excellent catalytic behavior owing to its large surface area and Lewis acidic nature at the metal nodes. Furthermore, UiO-66 showed excellent recyclability behavior, verified during repeated consecutive use in a sequence. The catalyst yielded similar catalytic behavior during the reduction of nitrophenols at each cycle, which is a novel finding.

Keywords: nano-metal organic frameworks (MOFs); UiO-66; catalyst; reduction reactions; reusability

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Synthesis of MIL-101(Fe)

A solvothermal method was used to synthesize MIL-101 (Fe-BDC). In a typical synthesis, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4 mmol, 0.80 g) and terephthalic acid (4 mmol, 0.67 g) were dissolved in 30 mL DMF, respectively. To speed up the dissolution process, an ultrasonic-assisted or stirring method was used. The two solutions were then transferred into a 100 mL Teflon-lined autoclave, and HF (0.8 mL, 5 M) was added. The resulting mixture was agitated for 10 minutes by using an ultrasonic instrument. Finally, the autoclave was placed in a 150 °C oven for 24 hours. The sample was centrifuged after being cooled to room temperature in air and washed with DMF, methanol, and water. The product was dried in a vacuum oven at 60 °C.

Synthesis of MOF-5 (Zn-BDC)

The Zn-BDC MOF (MOF-5) was synthesized by using Zinc acetate dihydrate (2.111 gm) (9.61 mmol) and 1,4-benzene dicarboxylic acid (0.631 gm) (3.8 mmol). These two precursors were dissolved individually in 30 ml of dimethylformamide (DMF) in a 60 ml glass vial in which 1.5 ml of triethanolamine was added drop-wise with constant stirring. The resulting mixture was ultra-sonicated for about 10 minutes for the uniform suspension of particles, transferred to a Teflon-lined autoclave, and placed in an oven at 90 °C for 24 hours. The reaction mixture was cooled to room temperature, then filtered off and washed three times with DMF and four times with CHCl_3 to remove the unreacted linker. The resulting as-synthesized material when dried under vacuum at 80 °C for 24 hours gives colorless sample.

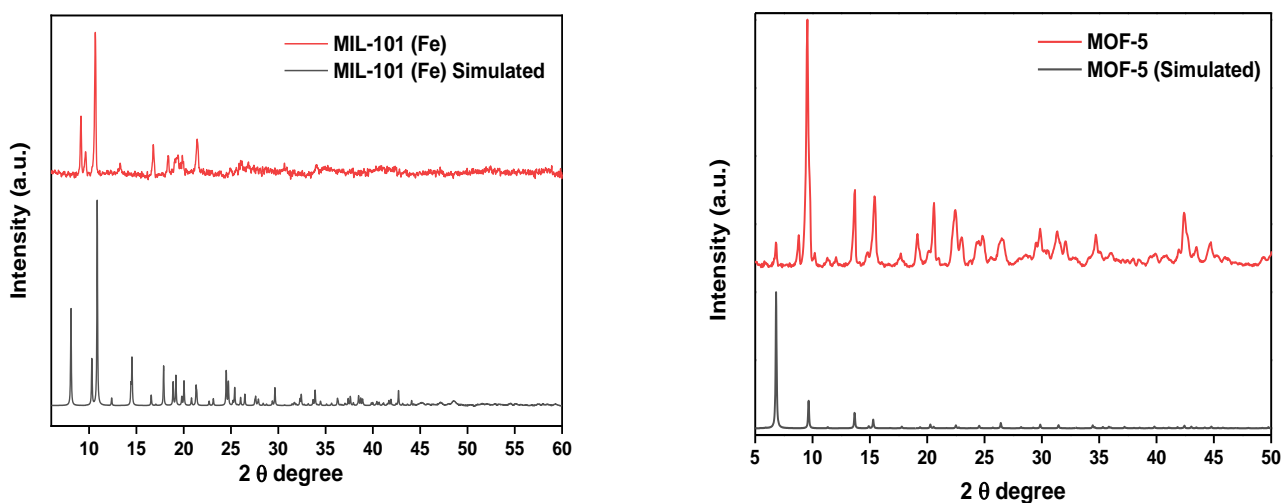


Figure S1. PXRD patterns of MIL-101(Fe) and MOF-5.

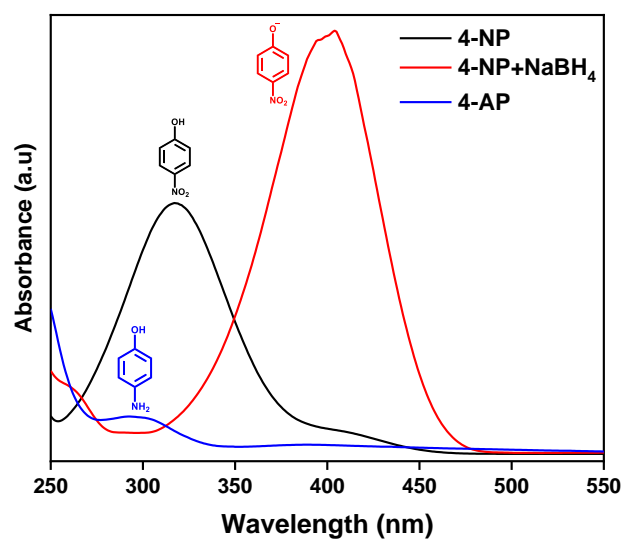


Figure S2. UV-vis spectra for 4-nitrophenol (black line) 4-nitrophenoxide (red line) and 4-aminophenol (blue line) in solutions.

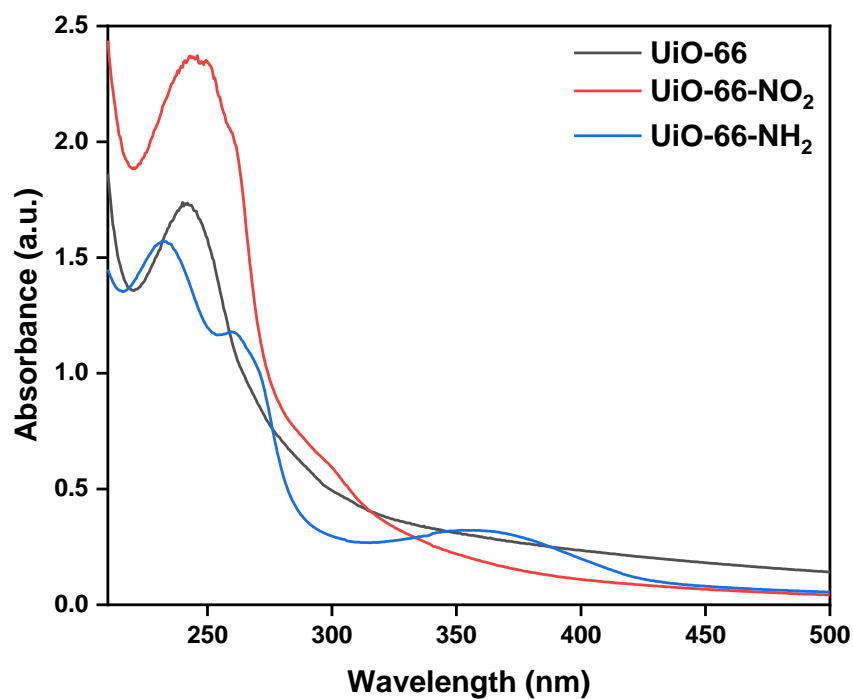


Figure S3. UV-vis spectra for UiO-66 (black line) UiO-66-NO₂ (red line) and UiO-66-NH₂ (blue line) in solutions.

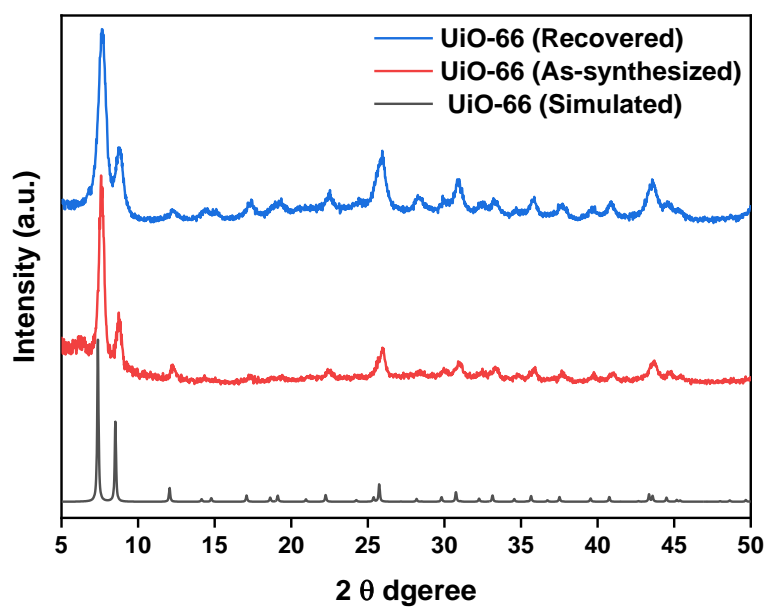


Figure S4. XRD of UiO-66 as-synthesized and after catalysis.

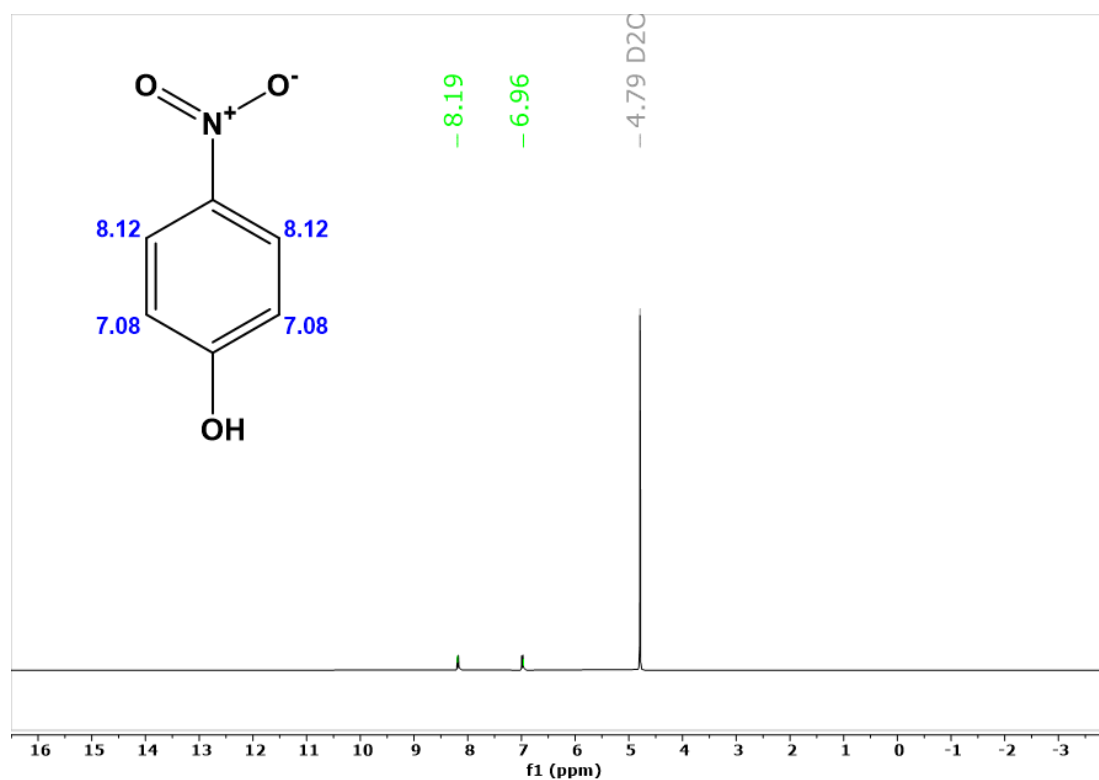


Figure S5. ^1H NMR spectra of reactant before the reaction showing the 4-NP peak.

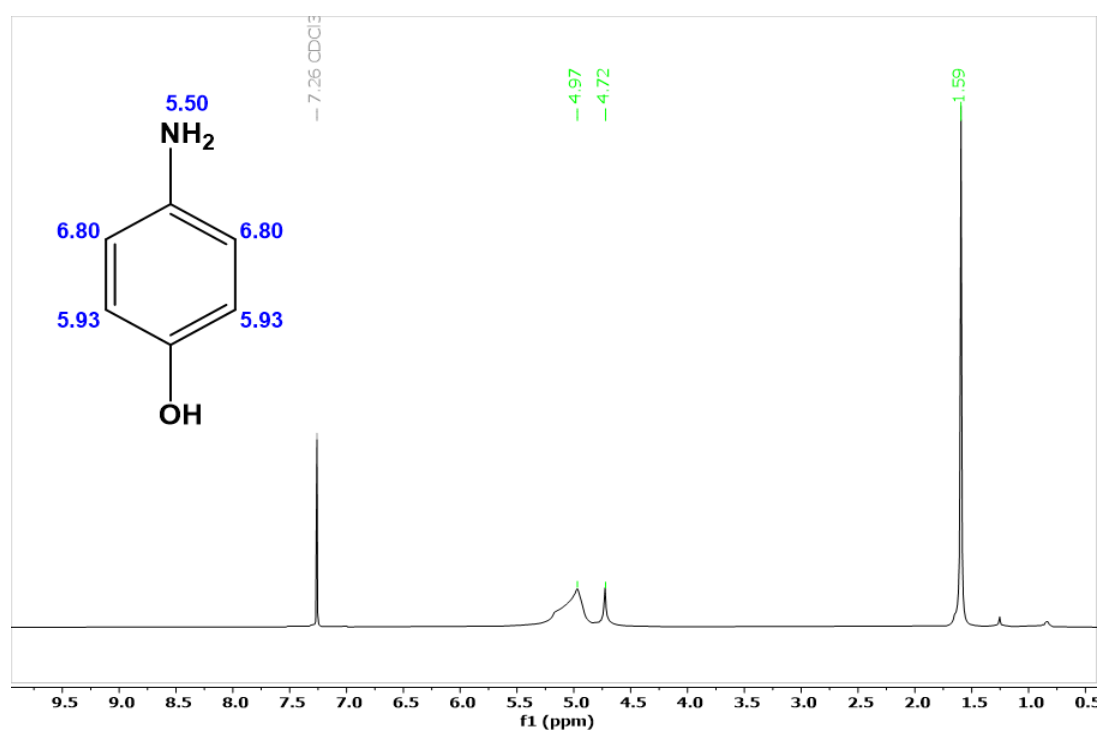


Figure S6. ¹H NMR spectra of product after the reaction showing the 4-AP peak using UiO-66 as catalyst

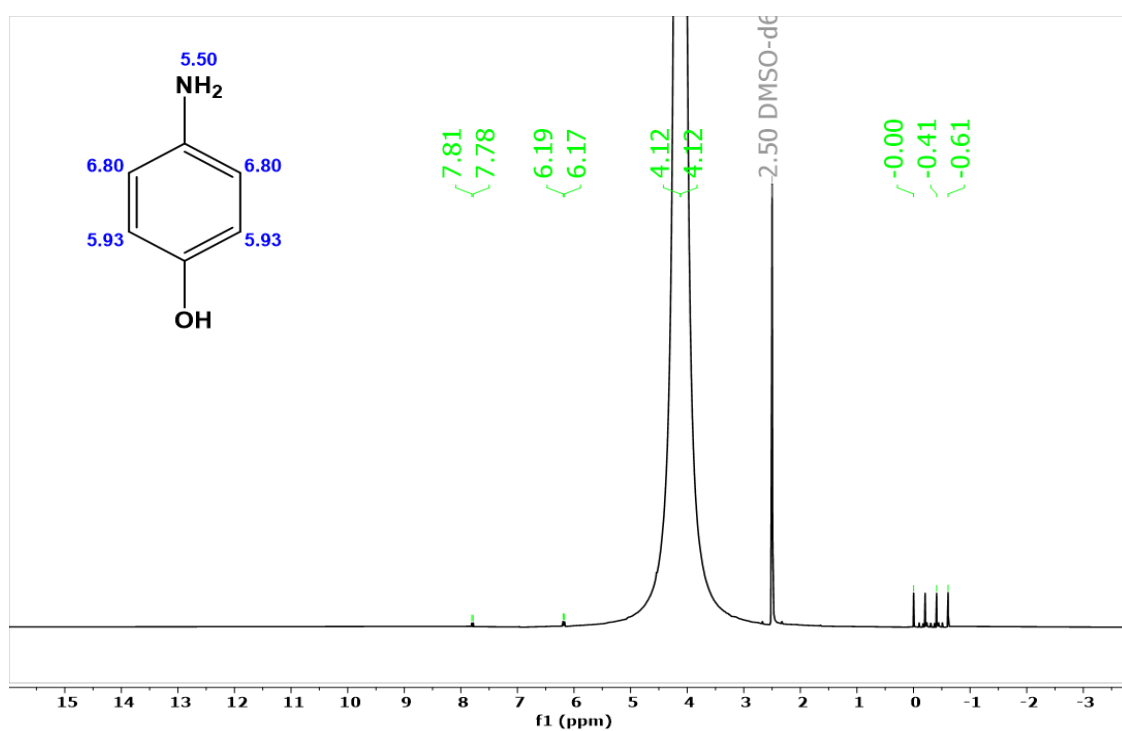


Figure 7. ¹H NMR spectra of product after the reaction showing the absence of 4-AP peak at (5.0 ppm) using UiO-66-NO₂ as catalyst.

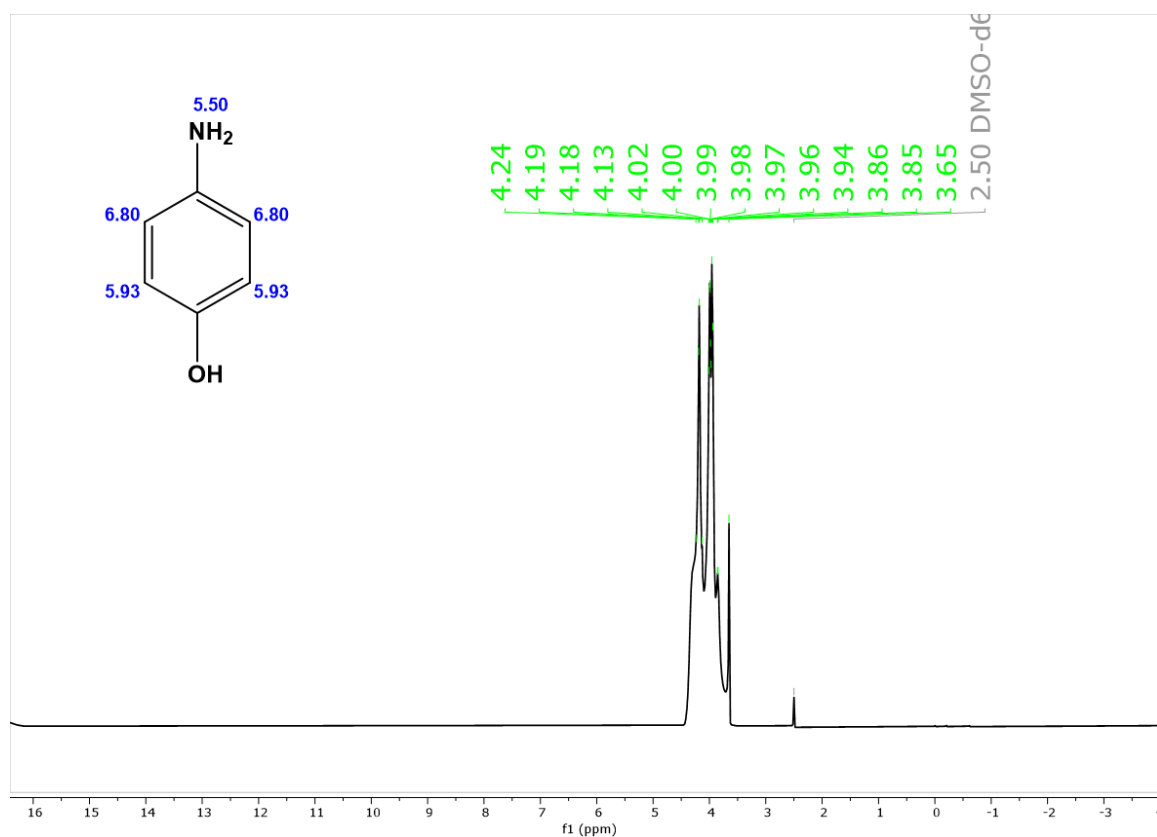


Figure S8. ^1H NMR spectra of product after the reaction showing the absence of 4-AP peak at (5.0 ppm) using UiO-66- NH_2 as catalyst.

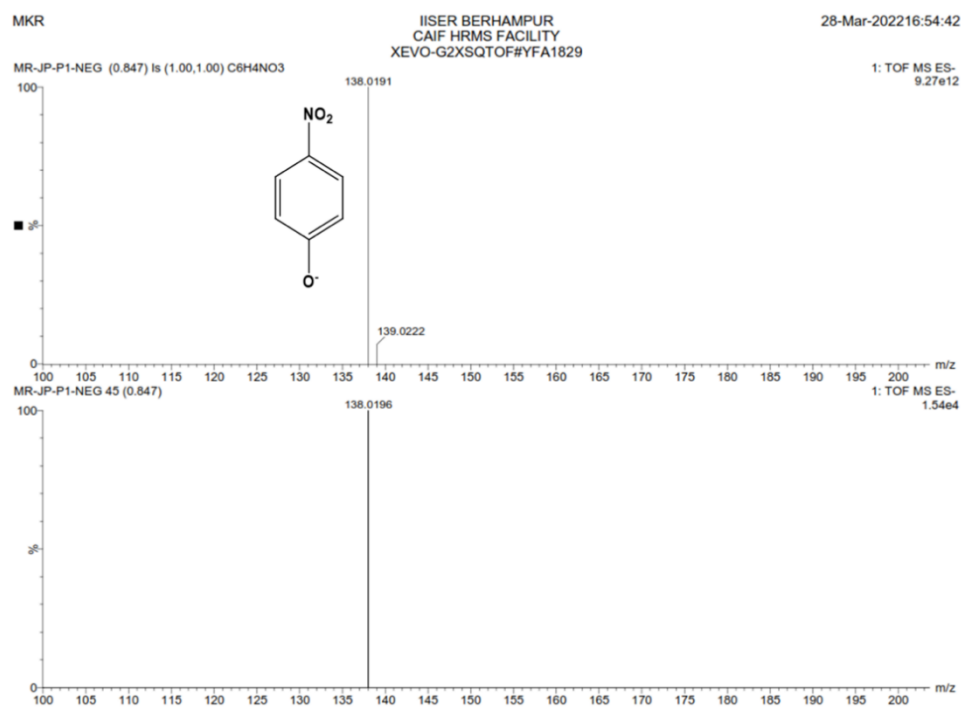


Figure S9. ESI-MS spectrum in negative ion mode of an aliquot taken before reaction in the presence of NaBH_4 and 4-NP.

