



Heterogeneous AgPd Alloy Nanocatalyst for Selective Reduction of Aromatic Nitro Compounds Using Formic Acid as Hydrogen Source

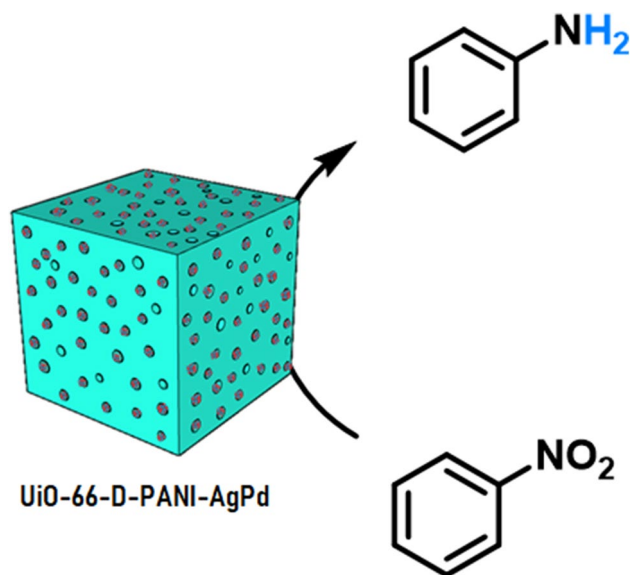
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Abstract

A Heterogeneous catalyst developed for selective reduction of nitroarenes to the analogous anilines using formic acid as hydrogen source. This catalytic procedure offers a simplistic path to prepare aromatic amines in good to excellent yields. Especially, even anilines functionalized with other potentially reducible moieties are obtained with high selectivity. Herein, we report convenient and stable bimetallic AgPd nanocatalyst supported on metal organic framework coated with polyaniline. Hydrogenation of nitroarenes gave analogues anilines with excellent yields at 90 °C in 6 h with no use of additives. Catalyst maintained stable performance in five repeated cycles.

Graphic Abstract



Keywords Metal organic framework · Polyaniline · Heterogenous catalysis · Chemoselective reduction · Hydrogenation

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1 Introduction

Aromatic primary amines (Ar-NH₂) are important feed stocks and essential ingredients for the synthesis of several pharmaceutical, agrochemicals, dye, polymer, pigments, fine chemicals and natural products [1–3]. The method generally used for the production of Ar-NH₂ is hydrogenation of functionalised aromatic nitro compounds using a stoichiometric

amount of reducing agents in presence of metal catalyst based on gold, palladium, rhodium, ruthenium, and iridium [4–6]. However, a disadvantage of commercially offered Pd catalysts is their lack of chemo-selectivity. These catalytic systems are unfortunately related with environmental issues or formation of enormous undesired by-products. Supplementary alteration of noble metals with suitable additives was essential to improve the selectivity, but not at cost of activity. While, the existence of other reducible functional groups in the nitroarenes creates the dual necessities of activity and selective reduction of nitro group pretty challenging. Leaching of metal from catalyst is also a major issue. The degree of leaching is strongly sensitive to the nanoparticle size, support material and most importantly reaction media and conditions. Although amazing improvements have been achieved but still the development of novel catalysts with broad functional group tolerance and high activity signifies an important challenge.

Recently, metal organic frameworks (MOFs) have established as a promising class of porous materials with very large precise surface area, high porosity, and chemical tunability [7]. Because of these advantages and facile synthesis of MOFs, have been accepted for common applications in many fields, including gas storage, gas separation, luminescence, drug delivery, and catalysis [8–12]. MOFs allow access to guest molecules similar to their pore size. A variety of approaches have been taken to create comparatively large pores in MOFs, including use of longer linkers, modulators, defective crystallization, and templates [13–18] but the silver-catalysed decarboxylation (silver etching) [7] is quite interesting. It creates heterogeneous pores, even in highly stable MOFs, without changing the unique structure. This alteration in MOFs generates meso porosity which can allow comparatively large guest molecules.

To defeat the leaching obstruction and to improve the performance of catalyst, alternative support materials must be developed to achieve high dispersion, utilization, activity, and stability. To fulfil these requirements intrinsically conducting polymer (ICP) class has attracted significant attention. After intensive research it is found that among all ICPs polyaniline (PANI) is a finest choice because of controllable conductivity, good chemical stability, high conductive property via doping with acids and, easy synthesis using tremendously simple chemical oxidation of the low price monomer (aniline) in aqueous solutions [19]. For PANI, It is expected that the N atoms in carbon matrix may not only act as an electron donor but also serve as anchoring sites for the precursor.

AgPd nanoparticles (NPs) are found to be promising in catalytic dehydrogenation of formic acid in aqueous medium [20–22]. The AgPd NPs was supported on metal organic framework for preparation of a heterogeneous nanocatalyst. To enhance the activity of catalyst MOF is firstly coated

with PANI. The catalytic enhancement is due to the synergic effect between Ag, Pd and PANI. The improved activity is because of electron delocalization between the d orbitals of Pd and the PANI π -conjugated ligand. The PANI coating also protects the MOF support from direct exposure to the corrosion and leaching. Several advantages of PANI coating is also there. First AgPd NPs supported on PANI is quite stable, furthermore the method of growing NPs is awfully simple. In this work a series of MOF composites were synthesized.

Herein, we reported heterogeneously catalysed selective reduction of nitroarenes using green reductant formic acid as the source of hydrogen. We synthesised MOF-PANI-Metal alloy composite (UiO-66-D-PANI-AgPd). In the first step, MOF (Zr based metal organic framework UiO-66) particles were prepared by hydrothermal route. MOF was decarboxylated by silver etching path. Then PANI was coated on the surface of decarboxylated MOF (UiO-66-D) by chemical (oxidative) polymerization method. In conclusion, AgPd nanoalloy grown on the PANI coated MOF surface.

1.1 Silver Etching Method

5 mL Acetonitrile solution of UiO-66 (100 mg), Potassium persulfate (135 mg, 0.5 mmol) and Silver nitrate (50 mg, 0.3 mmol) were allowed to react in Teflon-lined autoclave, and placed in a preheated silicon oil bath at 120 °C for 1 h. Decarboxylated MOF was centrifuged and washed three times with water and acetone. It was activated by keeping under vacuum for 1 h at 120 °C. This method was first introduced by Joeng et al. [7], they have described selective breaking of carboxylic bond during modification of MOFs, this will create pores in MOFs.

1.2 Preparation of Catalyst

Preparation of UiO-66-D-PANI-AgPd: Decarboxylated MOF (UiO-66-D) solution (250 mg, in 50 mL water) and Aniline solution (93 μ L, 1 mmol in 50 mL water with 5 mg Sodium dodecyl sulphate SDS) were sonicated separately for 1 h. Then both the solutions were mixed together on an ice bath and acidic solution of Ammonium persulfate (APS) (229 mg, 1 mmol in 25 mL 1 M HCl) was added drop wise with continuous stirring. Solution remained on stirring until green colour appeared. In this green suspension 10 mL aqueous solution of AgNO_3 (10% by weight of MOF) was added and stirred for 1 h. Further 10 mL aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (10% by weight of MOF) was added and stirred for another 1 h, followed by addition of Hydrazine hydrate (3 mL, 65%). Suspension was maintained at 90 °C for 4 h with stirring. Catalyst was collected by centrifugation, washed three times with water and acetone and finally activated by keeping under vacuum for 1 h at 120 °C.

2 Results and Discussion

To evaluate the efficiency and selectivity of catalyst, nitrobenzene was chosen as model substrate and solvothermal one-pot reactions (90 °C 6 h) between nitrobenzene and formic acid in aqueous medium was done. It is noted that Pd could be the main active component of the catalyst responsible for the selective hydrogenation. Recycled catalyst UiO-66-D-AgPd losing its efficiency because of leaching. We also observed that after loading PANI the results were enhanced. Furthermore, high selectivity of the catalyst was retained with no leaching through up to five cycles. Recycling via simple centrifugation with loaded NPs (Tables 1, 2).

2.1 Catalyst Characterization

AgPd NPs were synthesized from AgNO₃ and Pd(NO₃)₂ in water reducing by Hydrazine hydrate at 90 °C in 4 h. Figure 1 shows the XRD patterns of UiO-66-D-PANI-AgPd, UiO-66-D-AgPd and UiO-66-D. Similar to palladium, silver also has fcc structure with a cell constant of 0.40853 nm [23].















Decarboxylation of MOF confirmed by comparative IR data. Figure 2a, b provides the FTIR spectra of the decarboxylated MOF (UiO-66-D). It can be clearly seen that, after treatment with AgNO₃ and K₂S₂O₈ in Acetonitrile, intensity

Table 1 Comparative yields of nitrobenzene hydrogenation reactions with various synthesised catalysts

Entry	Catalyst	Yield (%)	
		2	3
1	UiO-66	NA	NA
2	UiO-66-D	NA	NA
3	UiO-66-PANI	NA	NA
4	UiO-66-D-PANI	NA	NA
5	UiO-66-Ag	NA	NA
6	UiO-66-D-AgPd	82	NA
7	Pd/C	74	13
8	UiO-66-PANI-AgPd	84	NA
9	UiO-66-D-PANI-AgPd	99	NA

Reaction conditions: Nitrobenzene (0.25 mmol), H₂O 1 mL, Formic acid (3 equivalent) catalyst 15 mg, temperature 90 °C for 6 h. Yield was determined by gas chromatography (GC-MS) analysis

Table 2 Chemoselective reduction of nitro group in various aromatic compounds

Reactant	Product	Yield %
		99
1 		93
2 		95
3 		91
4 		93
5 ^b 		90
6 		97

Reaction conditions: substrates (0.25 mmol), catalyst UiO-66-D-PANI-AgPd, formic acid (3 equiv.), H₂O (1 ml). Temperature 90 °C for 6 h. b-formic acid (6 equiv.) Yield is based on gas chromatography (GC-MS) analysis

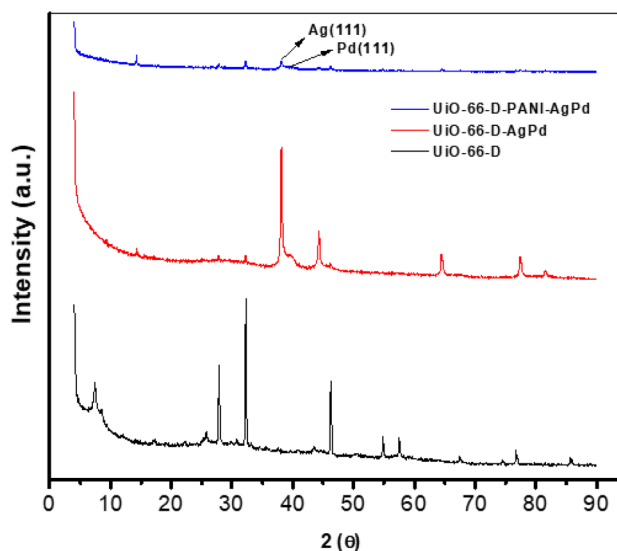


Fig. 1 Comparative XRD

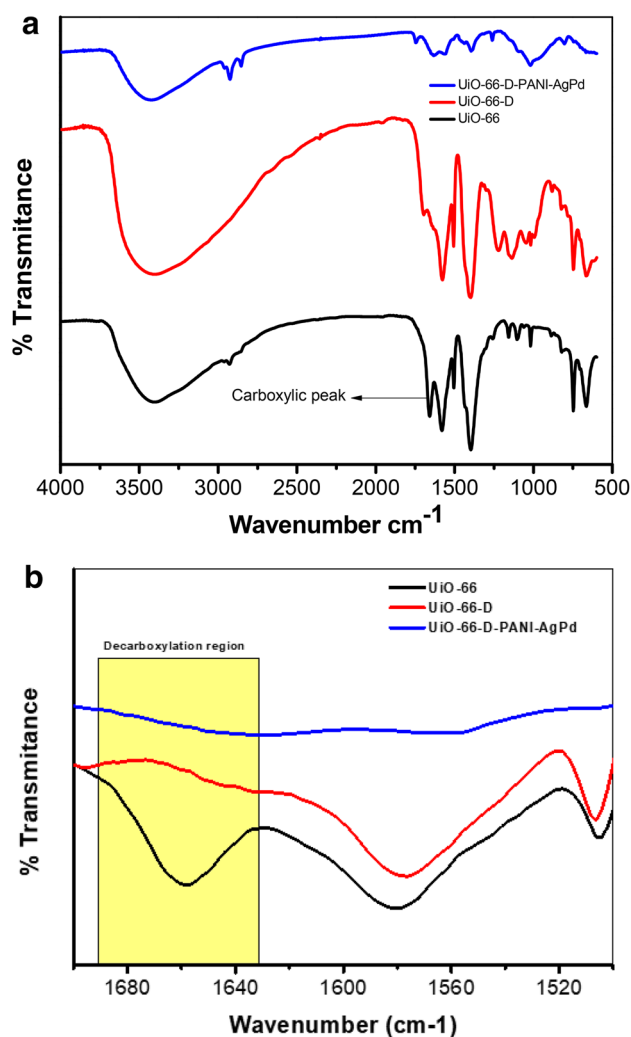


Fig. 2 a Comparative IR, b Comparative IR with specified peaks

of the peak at 1676 cm^{-1} belongs to the stretching vibration of carbonyl decreases [24].

3 Conclusion

We have introduced a novel heterogeneous catalyst UiO-66-D-PANI-AgPd for selective reduction of aryl nitro group. Our catalyst is effective in dehydrogenating formic acid to form H_2 and subsequently utilizing the hydrogen generated in situ for reduction of nitro group into amine. The catalyst is easy to synthesize, stable, easily separable, and readily recyclable without loss of activity, and the reactions can be carried out in water, making the process environmentally friendly.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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