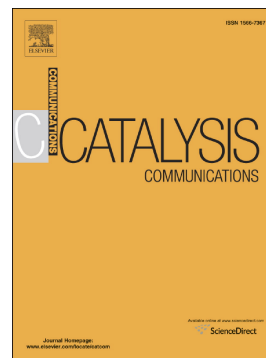


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PII: S1566-7367(17)30291-1
DOI: doi: [10.1016/j.catcom.2017.07.001](https://doi.org/10.1016/j.catcom.2017.07.001)
Reference: CATCOM 5120

To appear in: *Catalysis Communications*

Received date: 2 March 2017
Revised date: 13 June 2017
Accepted date: 4 July 2017

Please cite this article as: Yong Xu, Xiao-Jun Lv, Yong Chen, Wen-Fu Fu , Highly selective reduction of nitroarenes to anilines catalyzed using MOF-derived hollow Co₃S₄ in water under ambient conditions. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2017), doi: [10.1016/j.catcom.2017.07.001](https://doi.org/10.1016/j.catcom.2017.07.001)

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Highly selective reduction of nitroarenes to anilines catalyzed using
MOF-derived hollow Co_3S_4 in water under ambient conditions

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Abstract: We developed a new strategy for the efficient reduction of nitroarenes using sodium sulfide as reducing agent with MOF-derived Co_3S_4 as catalyst in water and at room temperature. The introduction of sodium sulfite enhanced the reactant conversion and product selectivity, and the as-synthesized catalyst was used repeatedly five times and retained its activity and selectivity. A wide spectrum of reducible functional moieties kept unaffected under the reaction conditions, and isotope labeling experiment showed the hydrogen atom was derived from water.

Keywords: Metal-organic frameworks; Hollow Co_3S_4 ; Nitro reduction; Heterogeneous catalysis; Sodium sulfide

1. Introduction

The development of a new kind of organic synthesis reaction is a big but worthwhile challenge. As a class of significant industrial chemicals, approximately 95% of nitroarenes are transformed into anilines, which are important precursors for the synthesis of pharmaceuticals, pesticides, dyes, rubber chemicals, and agricultural chemicals [1-4]. The pioneering work for the reduction of nitroarenes generally involved catalytic hydrogenation of the nitro group using precious metals such as Au, Pt, and Pd deposited on active carbon or metal-organic frameworks (MOFs) [5-8]. In addition to hydrogen, other reducing agents such as silane, ammonia borane, sodium borohydride, formic acid and hydrazine have been used to reduce nitroarenes in combination with metal-bearing catalysts [8-12]. Moreover, it is also a challenge to selectively reduce only the nitro group at a fast reaction rate while keeping any other reducible functional groups in the molecule unchanged. There have been a few reports on the use of sodium sulfide as a reductant, which is known as the Zinin Reaction. However, some byproducts such as aldehydes and condensation products of amines are found in this reaction using the model substrate p-methyl nitrobenzene (Fig. 1) [13-15].

(Embed Fig. 1 here)

Recently, noble-metal-free catalysts have caused extensive concerns for researchers, taking into account the cost and resource storage [16-18].

Especially, catalysts containing cobalt have attracted increasing attention as alternatives to replace noble-metal-based catalysts, owing to the low cost and remarkable catalytic activities for the reduction of water, dioxygen, carbon dioxide, and hydrogenation [19-22]. In comparison, metal-organic frameworks constructed from metal ions and polyfunctional organic ligands have become attractive and important materials in many fields due to their excellent physical and chemical properties such as low density, extra high specific surface area, and well defined pore structure [20, 23-24]. However, the fabrication of hollow nanomaterials with controlled morphology and composition is still a bottleneck. Interestingly, zeolitic imidazolate framework-67 (ZIF-67), a cobalt-based MOF, has been used as a self-templating precursor to prepare hollow Co_3S_4 through a solvothermal reaction with thioacetamide (TAA) and a thermal annealing process. The synthesized Co_3S_4 maintained a dodecahedral configuration and the special properties of MOFs including high conductivity and thermal stability over a broad pH range from 0 to 14 [25]. To the best of our knowledge, we demonstrate for the first time that this material also displays excellent activity for the catalytic reduction of nitroarenes to anilines without any disproportionation or condensation products by using sodium sulfide as a reductant in the presence of sodium sulfite.

2. Experimental

2.1. Preparation of hollow Co_3S_4

To prepare Co_3S_4 , first, ZIF-67 was synthesized based on previous report with some

modifications. Typically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.74 g) was dissolved in 30 mL of methanol. Another solution containing 3.94 g 2-methylimidazole was rapidly added to the above solution with violently stirring for 1 min. Then the mixture was kept for 24 h at room temperature. Deep purple ZIF-67 products were obtained by centrifugation and washed with water and ethanol three times, followed by vacuum drying at 60 °C overnight.

For the preparation of hollow Co_3S_4 , 80 mg as-produced ZIF-67 was dispersed into 20 mL of ethanol accompanied with ultrasonic irradiation for 20 min. 0.12 g TAA was dissolved in another 20 mL of ethanol, which was poured into ZIF-67 mixture. The obtained mixture was transferred into 50 mL autoclave, heated and kept at 120 °C for 6 h. The produced sulfide was centrifuged, washed with ethanol three times and dried at 70 °C in vacuum oven. The sample was heated at 350 °C for 2 h in tube furnace with a heating rate of 3.3 °C/min under Ar atmosphere.

2.2. Preparation of ordinary Co_3S_4 (o- Co_3S_4)

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (582 mg) and TAA (751.3 mg) were dissolved in 40 mL of ethanol. The process followed is similar to that of hollow Co_3S_4 .

2.3. Catalytic reduction of nitroarenes

Typically, 5 mL $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ aqueous solution containing 0.4 mmol substrate and 5 mg hollow Co_3S_4 was added into 15 mL cuvette sealed with a rubber septum. A stream of Ar was bubbled into the reaction system for 10 min and then the reaction solution was stirred with a magnetic stirrer at room temperature. In order to reduce random error, the position of cuvettes was swapped every half an hour.

Dichloromethane was used as extraction agent and extracted 3 times in a row with p-xylene as internal standard. Products were characterized by NMR analysis (ESI).

3. Results and discussion

The as-synthesized hollow Co_3S_4 was characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), elemental mapping, and energy dispersive X-ray (EDX) spectroscopy (Fig. 2 and S1). The XRD pattern corresponds to cubic Co_3S_4 (JCPDS No. 47-1738). SEM and TEM images provide details of the exterior and interior of the hollow structure, which demonstrates a sharp contrast of the MOF's morphology between the center and the edge. The lattice spaces of 0.285, 0.236, and 0.168 nm are ascribed to the (311), (400), and (440) planes. EDX analysis (Fig. S1(I)) reveals an approximate Co/S ratio of 3:4 based on the calculated peak areas, confirming the successful formation of the desired catalyst. The Si peak come from the silicon pellet. EDX mapping further reveals that all elements are uniformly distributed in the Co_3S_4 . As shown in Fig. S2, X-ray photoelectron survey spectra of Co_3S_4 shows low-energy peaks with binding energies of 778.4 and 780.0 eV, corresponding to Co $2p_{3/2}$ state, while high-energy peaks at 793.2 eV, 796.8 eV were assigned to Co $2p_{1/2}$ states. The first doublet at 778.4 eV, 793.2 eV and the second at 780.0 eV, 796.8 eV were assigned to Co^{2+} and Co^{3+} , respectively. A broaden peak (801.8 eV) at higher binding-energy can be attributed to satellite signal.

(Embed  Fig. 2 here)

Initially, the reduction reaction was performed using p-methyl nitrobenzene as the model substrate with sodium sulfide as the reductant and water as the hydrogen source at room temperature (Table 1). After stirring for 10 h with the hollow Co_3S_4 catalyst, the conversion and selectivity were 65.4 % and 73.5 % in the absence of Na_2SO_3 , respectively. However, both the conversion and selectivity almost reached 100 % after stirring for 6 h in the presence of sodium sulfite. The results demonstrated that present catalytic system could be used to reduce the nitro group to an amino group without heating. Interestingly, the nitro group could not be reduced using only sodium sulfite as the reducing agent (Table 1, entry 3). Control experiments showed that the reduction reaction could not be conducted in the absence of Co_3S_4 or sodium sulfide. Control experiments showed that other sacrificial agents, including formic acid, triethanolamine (TEOA), and isopropanol, could not be used for reduction of the nitro group. In contrast, the conversion was only 12.1 % after stirring for 6 h when ordinary Co_3S_4 (o- Co_3S_4) was also used as catalyst (Table 1, entry 6, 7).

(Embed Table 1 here)

The results showed that sodium sulfite had a significant influence on both the conversion and selectivity of the reduction reaction. To investigate the effect of the sodium sulfide concentration on the reaction rate and to optimize the catalytic reaction conditions, a series of experiments were performed by varying the ratio of sodium sulfide and sodium sulfite while maintaining the

concentration of sodium sulfite. As shown in Fig. 3, after stirring for 3 h, a selectivity of up to 100 % for the reduction of p-methyl nitrobenzene to aniline was achieved when the concentration of sodium sulfide was relatively small. As the sodium sulfide content increased, the selectivity gradually declined whereas the conversion increased. This indicated the acceleration of the reaction as a result of increasing sodium sulfide concentration, but the catalytic activity at higher sulfide concentrations slightly decreased. This can be related to the effects of sulfur anion oxidated to elemental sulfur on reaction rate in the process of substrate conversion, which is loaded on the surface of dodecahedral Co_3S_4 , decreasing the active sites of catalyst. Generally, the reduction of nitrobenzene to aniline processes three steps, i. e. from nitrobenzene to nitrosobenzene and to N-phenylhydroxylamine intermediates, then to formation of product. Furthermore, cobalt has a high affinity to the nitro group compared with the nitroso only having one oxygen atom, the generated nitrosobenzene easily detach from the catalyst [26-28]. Higher sulfide concentration will lead to accumulation of nitrosobenzene in system and subsequent formation of a side product through a condensation reaction of it and N-phenylhydroxylamine [29]. The optimal $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ molar ratio was determined to be 5:7.

(Embed Fig. 3 here)

In comparison, no product was obtained if 1 atm of H_2 was used as the reductant, which suggested that activated hydrogen species could be involved in the reduction. Based on previous studies, traditional metal-based catalysts

such as Pd loaded on solid support transfer hydrogen to generate atomic hydrogen on the surface of the catalysts and reduce organic compounds by using sacrificial agents [11, 30]. Analogously, metallic Co_3S_4 displays the function, transferring hydrogen from water to form $\text{H-Co}_3\text{S}_4$ species on its surface, which is the key for the promotion of the whole reaction. In accordance with our conjecture, an investigation was performed to verify the existence of this species in the absence of nitroarenes. As expected, a small amount of H_2 gas was detected using gas chromatography in a system containing an aqueous solution of Na_2S , Na_2SO_3 , and Co_3S_4 after stirring for 4 days. Isotope labelling experiment was also conducted using deuterium oxide instead of water and the result gained revealed that N-D bond formed in the reduction (Fig. S3).

The nitro group could coordinate to the cobalt center of the catalyst surface during the nitroarene reduction process, as reported previously [28]. Before the evolution of dihydrogen, the hydride generated on the surface of Co_3S_4 could transfer hydrogen of water to the coordinated nitroarenes. In 1898, Haber first put forward the well-known reduction pathways, that is, a stepwise pattern via nitroso and hydroxylamine intermediates, which may condense to coupling compounds such as azoxybenzene and azobenzene [31]. However, the reaction procedure for the reduction of an azoxy to an azo and to aniline group was less efficient. In the eyes of the mechanism, the coordinated nitro group was hydrogenated to nitroso and hydroxylamine groups, followed by their coupling products (Fig. S4) [29]. The results were further confirmed by the decreasing

selectivity as the proportion of sodium sulfide was increased (Fig. 3). The selectivity increased from 88.1% ($\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ molar ratio of 5:7, stirring for 3 h) to 99.8% (Table 1, entry 2) by prolonging the reaction time. To gain further insight into the reaction pathways, the reduction of the condensation product, azobenzene was used as substrate, was worked out, keeping the experimental conditions identical to those for the reduction of nitroarenes. The obtained results demonstrated that hydrazobenzene was the only product after stirring for 2 days (ESI). However, the details of the mechanism are still unclear, and more studies are needed to gain a better understanding of the mechanism.

The catalytic system was generally applicable for the reduction of other nitroarenes. Dehalogenation of sensitive halogen-containing nitroarenes was expected to occur, as previously reported [32]. However, halogenated nitroarenes were reduced to afford the corresponding anilines with excellent selectivity and suppression of dehalogenation in our system (Table 2, entry 9, 10). From a synthetic point of view, it is challenging to selectively reduce nitroarenes functionalized with other reducible moieties to valuable anilines at a fast reaction rate. In this catalytic system, selective hydrogenation of the nitro group was performed in the presence of vulnerable functional groups such as aldehyde, ketone, cyano, amides and esters (Table 2, entry 1, 2, 11-13). The activity of 4-nitrobenzotrile was the lowest compared with other substrates. Furthermore, the conversion and selectivity of nitroarenes containing electron-withdrawing substituents was lower than those containing

electron-donating groups. This indicates that substrates bearing electron-donating groups may be more difficult to detach from the surface of the catalyst compared with those containing electron-withdrawing groups. Taking steric hindrance effect into consideration, bulky substituents impede intimate contact between the substrate molecules and the catalyst, resulting in poor catalytic activity in the catalytic reduction reaction (Table 2, entry 5, 8).

(Embed Table 2 here)

The reusability of hollow Co_3S_4 catalyst was examined by reducing p-methyl nitrobenzene to the corresponding p-methyl aminobenzene without any regeneration, which is very critical for industrial applications. As shown in Fig. 4, the catalyst was collected by centrifugation and repeated washing with deionized water and ethanol, and subsequently dried at 70 °C in an oven. The activity of the catalyst was retained after five successive runs without any obvious decrease in conversion, selectivity and yield. XRD pattern after 5 cycles maintains the crystal phase of Co_3S_4 (Fig. S5) but some hollow dodecahedrons are falling apart (Fig. S6).

(Embed Fig. 4 here)

4. Conclusion

In summary, MOF-derived hollow Co_3S_4 was used as an excellent catalyst in an aqueous solution of sodium sulfide with sodium sulfite for the reduction of nitroarenes to anilines without the need for intensive heating. The introduction of sodium sulfite to the catalytic system was essential for obtaining high

conversion and selectivity. High chemoselectivity was achieved during the reduction of nitroarene substrates containing other reducible functional groups. Isotope labeling experiment showed the hydrogen atom was derived from water. Co_3S_4 could be recycled five times and maintained high catalytic activity. This strategy represents a new train of thought for the reduction of nitro compounds.

Acknowledgements

This work was financially supported by the National Key Basic Research Program of China (973 Program 2013CB834804) and the Ministry of Science and Technology (2012DFH40090) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17030200). We thank the National Natural Science Foundation of China (21267025, 21471155, 21367026) for financial support.

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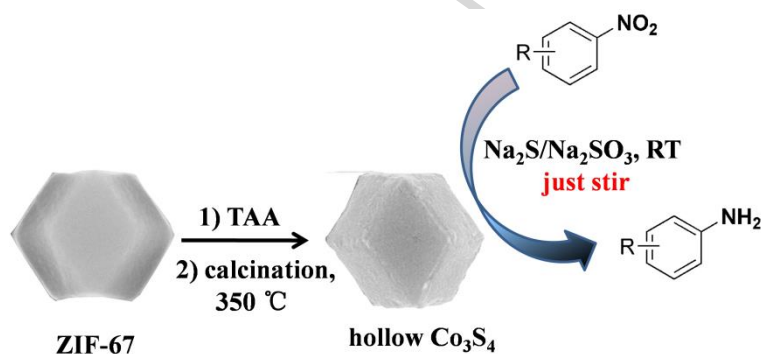
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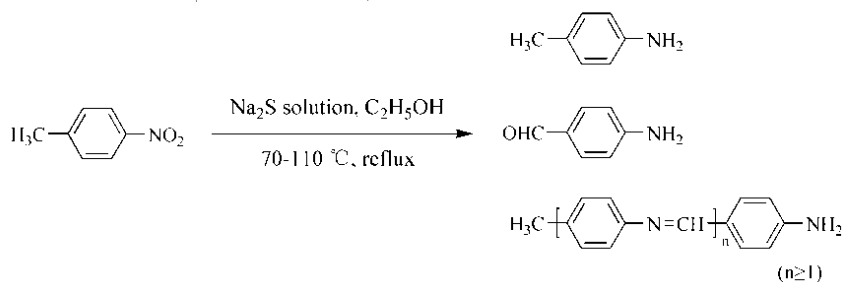
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Graphical Abstract

MOF-derived hollow Co_3S_4 introduced reduction of nitroarenes to anilines efficiently using sodium sulfide as reductant with sodium sulfite in water.



Previous studies (Zinin Reaction)



This work

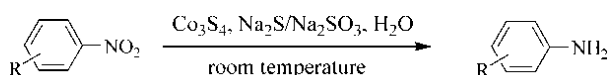


Fig. 1. Schematic illustration of the strategies for the reduction of nitroarenes.

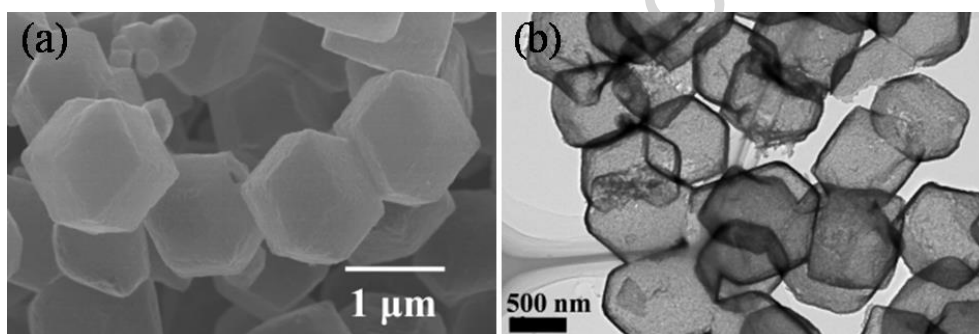


Fig. 2. (a) SEM and (b) TEM images of Co_3S_4 .

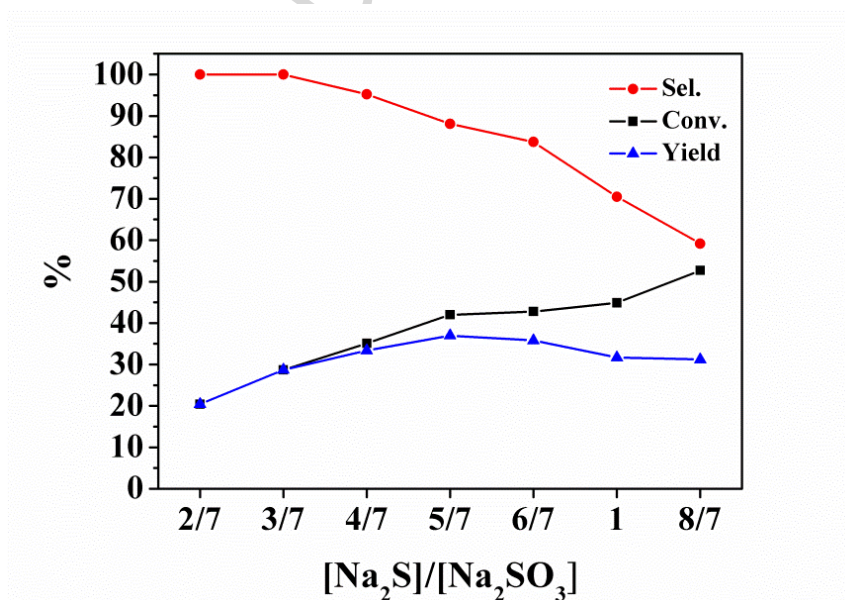
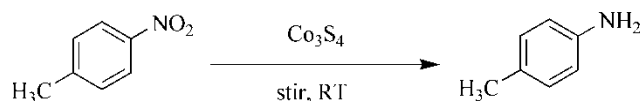
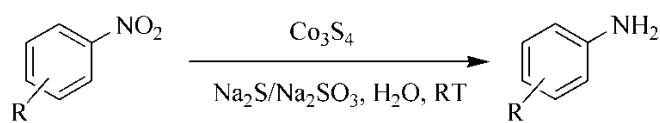


Fig. 3. Changes of conversion, selectivity and yield depending on the concentration ratio of sodium sulfide and sodium sulfite at room temperature. Reaction conditions: 0.4 mmol p-methyl nitrobenzene, 5 mg Co_3S_4 catalyst, 5 mL of H_2O , fixed concentration of Na_2SO_3 (0.35 M), stirring for 3 h.



Entry	Reductant	Conv. (%)	Sel. (%)	Yield (%)	TOF (h ⁻¹)
1 ^a	Na ₂ S	65.4	73.5	47.4	1.60
2 ^b	Na ₂ S/Na ₂ SO ₃	100	99.8	99.8	4.07
3 ^a	Na ₂ SO ₃	0	—	0	0
4 ^c	—	0	—	0	0
5 ^d	Na ₂ S/Na ₂ SO ₃	0	—	0	0
6 ^e	Na ₂ S/Na ₂ SO ₃	5.0	99.6	5.0	0.41
7 ^f	Na ₂ S/Na ₂ SO ₃	12.1	99.3	12.0	0.49

Table 1. Catalytic reduction of p-methyl nitrobenzene with hollow Co₃S₄ and sodium sulfide at room temperature. Reaction conditions: 0.4 mmol p-methyl nitrobenzene, 5 mg Co₃S₄ catalyst, 5 mL H₂O, Na₂S (0.25 M), Na₂SO₃ (0.35 M), ^astirring for 10 h; ^bStirring for 6 h; ^cWithout sodium sulfide and sodium sulfite; ^dIn the absence of hollow Co₃S₄; ^eo-Co₃S₄ was used as catalyst, stirring for 3 h and ^f6 h.



Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1			2.5	100	>99.9
2			2.5	100	>99.9
3			3.5	100	>99.9
4			4	98.0	>99.9
5			4	90.9	>99.9
6			4	98.2	91.7
7			4	100	51.0
8			4	87.7	>99.9
9			4	92.9	>99.9
10			4	90.0	>99.9
11			4	68.9	88.5
12			4	67.0	54.6
13			2	95.1	98.0

Table 2. Reduction of substituted nitroarenes to produce anilines in our catalytic system. ^aReaction conditions: 0.2 mmol substrate, 5 mg Co₃S₄ catalyst, 5 mL of H₂O, Na₂S (0.25 M), Na₂SO₃ (0.35 M), stirring at room temperature.

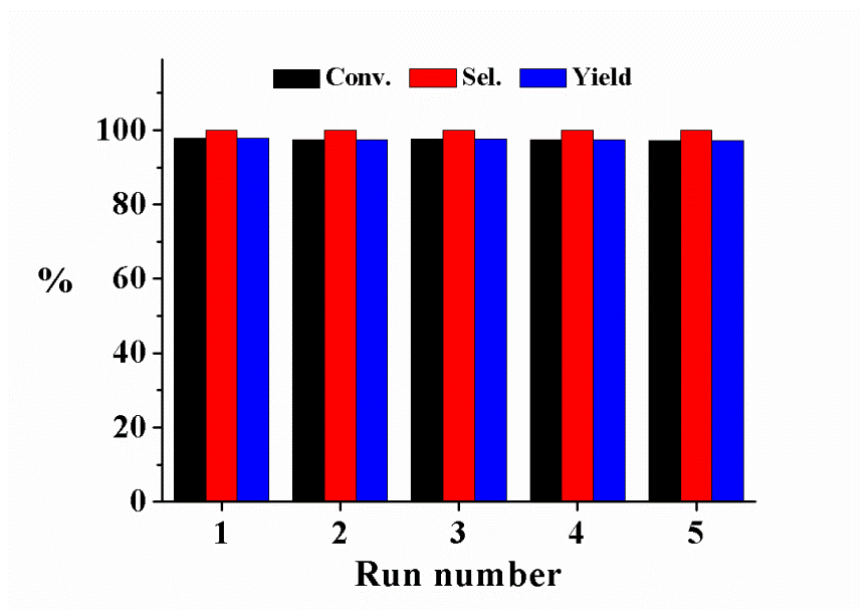


Fig. 4. Reutilization of Co_3S_4 catalyst for nitroarenes reduction. Reaction conditions: 0.4 mmol p-methyl nitrobenzene, 5 mg Co_3S_4 catalyst, 5 mL solvent, Na_2S (0.25 M), Na_2SO_3 (0.35 M), stirring 5 h, at room temperature.

Highlights

- MOF as a precursor to prepare hollow Co_3S_4 with dodecahedral configuration
- Co_3S_4 introduced reduction of nitroarenes to anilines keeping reducible groups
- MOF-derived Co_3S_4 having highly catalytic efficiency
- Sodium sulfide used as reductant without requiring heating in aqueous solution