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FULL PAPER

Metal organic framework-capsulated CoCu nanoparticles for the selective transfer hydrogenation of nitrobenzaldehydes: engineering active armour by half-way injection method

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Dedication ((optional))

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Abstract: A novel armour-type composite of metal organic framework-capsulated CoCu nanoparticles with Fe_3O_4 core (Fe_3O_4@SiO_2-NH_2-CoCu@UiO-66) has been designed and synthesized by the half-way injection method, which successfully serves as an efficient and recyclable catalyst for the selective transfer hydrogenation. In this half-way injection approach, the pre-synthetic Fe_3O_4@SiO_2-NH_2-CoCu was injected into the UiO-66 precursors solution halfway through the MOF budding period. The formed MOF armour could play a role of providing momentous additional catalytic sites besides CoCu nanoparticles, protecting CoCu nanoparticles and improving the catalyst stability, thus facilitating the selective transfer hydrogenation of nitrobenzaldehydes into corresponding nitrobenzyl alcohols in high selectivity (99%) and conversion (99%) rather than nitro group reduction products. Notably, this method achieves the precise assembly of MOF-capsulated composite, and the ingenious combination of MOF and nanoparticles exhibits excellent catalytic performance in the selective hydrogen transfer reaction, implementing a "1+1>2" strategy in catalysis.

Introduction

Metal-organic frameworks (MOFs) have attracted extensive attention because of their unique properties including high specific surface area, high porosity[1] and structural variability.[2] Recently, many efforts on combining of MOFs and other functional components to fabricate composite materials with new excellent properties have been devoted.[3] Compared with single component of MOFs, composite materials involving MOFs with multi-functional sites can show new application prospects in the fields of gas storage,[4] optics and electrical conductivity,[5] chemical separation,[6] sensing,[7] drug delivery[8] and especially catalysis.[9] In particular, metal nanoparticles, possessing large contact area per unit volume and uniform metallic active centers can be employed to composite with MOFs. And the cage structure from MOF can serve as an armour to encapsulate the supported metal nanoparticles into MOFs, which will disperse and stabilize the nanoparticles to prevent them from shedding and agglomeration, thus promoting the superior catalytic activity,[10] enhancing the recycling performance.[11] More importantly, MOFs can also be considered as a selective regulation. When using a porous material with clear pore characteristics, the division between the external and internal pore structures and the competitive adsorption effect can work as gates to potentially control the catalytic and reactive sites for some selective organic reactions.[12]

Catalytic transfer hydrogenation (CTH) refers to using a hydrogen donor as a source of hydrogen to perform a reaction on a hydrogen acceptor.[13] Compared with the external hydrogenation method, the CTH reaction exhibits advantages of mild reaction conditions, safe and facile manipulation and broad application of reductive products, etc.[14] In the CTH system, as one of the mild and green solvents, isopropyl alcohol (IPA) can be regarded as a hydrogen donor for CTH, with the merits of high hydrogen production capacity and medium boiling point,[15] and the medium boiling point contributes to the efficient separation of products.[16] Particularly, indirect CTH is beneficial to control the degree of the hydrogenation and avoid the formation of by-products caused by excessive hydrogenation[17] or insufficient hydrogenation. Among all the reactive pathways, the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols is an attractive process for the synthesis of chemical intermediates, widely applied in the production of pharmaceuticals, cosmetics and food. Especially, unsaturated aldehydes containing nitro group has a strong electron deficiency and the addition of hydrogen to the nitro is usually thermodynamically and favoured over the aldehyde groups. Therefore, it is challenging and desirable to achieve the selective hydrogenation on the aldehyde group with the nitro group intact.Considering the combined catalytic advantages of metal nanoparticles and MOFs, the development of effective encapsulation has become the key strategy to construct the

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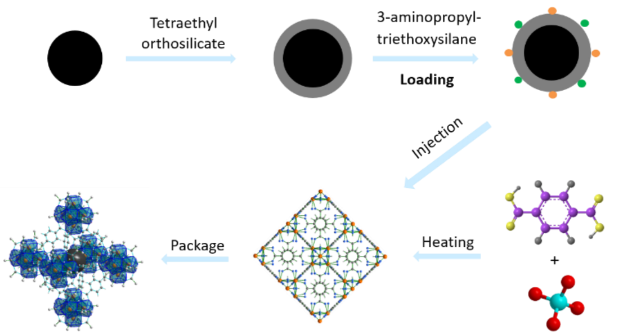


Scheme 1. The preparation of armour-type $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66 composite nano-catalyst

selective gate.[18] According to our previous work,[19] CoCu nanoparticles can be dispersed and supported on the core of $Fe_3O_4@SiO_2$-NH_2, which may be regarded as the preliminary preparation for the further compositing. Here, MOF can be designed to capsulate the supported CoCu nanoparticles, whose composite structure could provide synergistic catalytic sites and potential selective gate for the hydrogenation of unsaturated aldehydes. Therefore, in this work, we explored a half-way injection method (Scheme 1), that is injecting metal nanoparticles prepared in advance during the budding period of MOF formation to dexterously form an active armoured catalyst of metal organic framework-capsulated CoCu nanoparticles with $Fe_3O_4@SiO_2$ core. Both the MOF armour and CoCu nanoparticles center can offer active catalytic sites, efficiently catalyzing the selective transfer hydrogenation of aldehyde groups to corresponding alcohols rather than the hydrogenation of nitro groups to amines, which achieves the “1+1>2” effect in catalysis.

Results and Discussion

The armour-type catalyst $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66 could not be synthesized effectively by traditional hydrothermal synthesis method. When the two parts of the core and shell were added in a physically mixed manner, there would be no armour shell formation (Figure S1). Moreover, the metal nanoparticles were easy to peel off without the protection of MOF, and the recycling efficiency was greatly reduced. Based on our above attempts, we tried a half-way injection method by injecting pre-synthetic metal nanoparticles during the budding period of MOF formation, thus dexterously forming an active armoured catalyst of metal organic framework-capsulated CoCu nanoparticles with $Fe_3O_4@SiO_2$ core. In Figure 1(a), $Fe_3O_4@SiO_2$-NH_2-CoCu could be observed in transmission electron microscopy (TEM) image. The interface between Fe_3O_4 and the silicon dioxide layer was clear and the contrast was high, indicating that the iron microsphere was successfully wrapped with a silicon layer with the thickness of 20 nm. Figure 1(f) showed the X-ray diffraction pattern of $Fe_3O_4@SiO_2$-NH_2-CoCu. The several sharp diffraction peaks at 2θ = 30.2 °, 35.6 °,43.1 ° 57.1 ° and 62.7 ° could be attributed to the (220), (311), (400), (511) and (440) planes of Fe_3O_4, respectively. And another set of diffraction peaks, centred at 50.1 °, 58.2 ° and 51.2 °, 60.3 °, index as Cu and Co element, respectively. The XRD results were consistent with the mapping images. After the capsulation by the MOF shell, the outermost layer of armour-type catalyst $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66 showed an octahedral shape as Figure 2(a). The results were consistent with the X-ray photoelectron spectrum (Figure S2) and the addition of the core did not destroy the structural characteristics of UiO-66 in octahedron in Figure 2(c).

Figure 3(a) showed the X-ray diffraction pattern of the as-synthesized $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66. The several

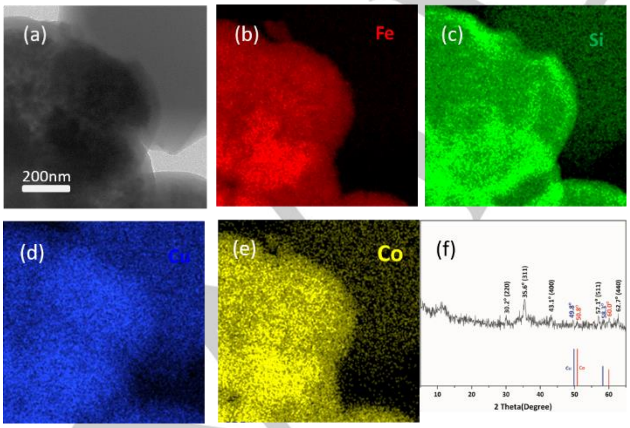


Figure 1. (a) TEM images of $Fe_3O_4@SiO_2$-NH_2-CoCu. (b-e) Elemental mapping of $Fe_3O_4@SiO_2$-NH_2-CoCu, (b) Fe, (c) Si, (d) Cu and (e) Co nanoparticles. (f) The XRD pattern of $Fe_3O_4@SiO_2$-NH_2-CoCu.

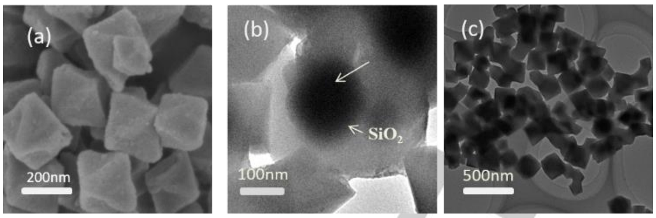


Figure 2. (a) SEM image and (b), (c) TEM images of $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66.

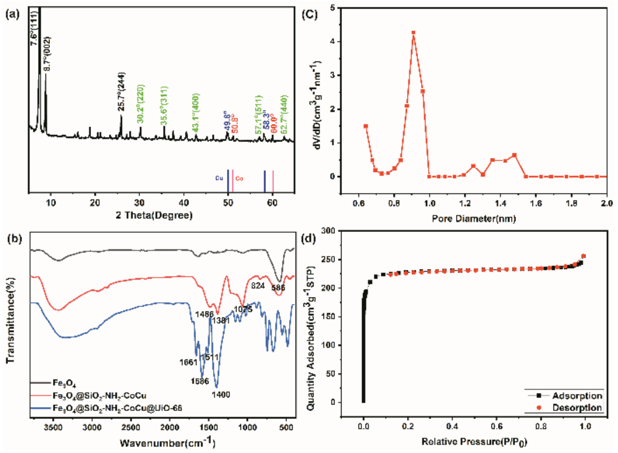


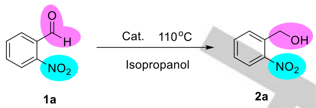
Figure 3. (a) XRD pattern of $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66. (b) FT-IR spectra, (c) Size distribution and (d) Nitrogen adsorption–desorption isotherm of $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66.

sharp diffraction peaks at 2θ = 7.6 °, 8.7 ° and 25.7 ° could be attributed to the (111), (002) and (244) planes of UiO-66, respectively,[20] which further demonstrated the successful synthesis of UiO-66 crystals' capsulation.

The successful preparation of the armoured structure $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$ could also be verified by Fourier transform infrared spectroscopy (FT-IR) in Figure 3(b). From the spectrum of Fe_3O_4 microspheres, it could be observed the adsorption peaks at 586 cm^{-1}, assigning to the functional groups of Fe-O bonds. For $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu$, the distinct IR spectral bands situated at 1075 cm^{-1} and 824 cm^{-1} were related to the asymmetric stretching vibration modes of Si-O-Si, and tensile vibration modes of Si-O, respectively. Meanwhile, two typical peaks at 1381 cm^{-1} and 1486 cm^{-1} could confirm the existence of $–NH_2$ groups. For $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$, the typical frame vibration absorption of benzene ring of UiO-66 could be recorded at 1586 cm^{-1}, 1511 cm^{-1} and 1400 cm^{-1}, and the peak at 1661 cm^{-1} proved the presence of carboxylic acid. The pore size was mainly distributed at 0.9 nm or so in Figure 3(c) and the surface area of the material was 1250 m^2g^{-1}, whose micropores resulted from the successful packaging of UiO-66, thus improving the surface area and porosity of the catalyst. Figure 3(d) showed the N_2 sorption isotherms, in which the armour-type catalyst showed isothermal curve of type I with a microporous structure.

In the process of catalytic performance test, considering that synergetic bimetallic components would increase the activity of the catalytic center, we tried a series of magnetic bimetallic nanoparticles catalysts for this selective transfer hydrogenation of 2-nitrobenzaldehyde in the early stage (Table 1). The bimetallic nanoparticle catalysts such as FeNi and FeCu did not have catalytic advantages in this system, but it was found that the combination effect of CuCo was effective for this selective reaction. Compared with single-component Co_3O_4, it indicated that the Co element played an important role, and the catalyst containing cobalt could promote the production of hydrogen.[21] However, the catalyst activity of CoNi was not ideal, but the combination of CoCu showed better effect, so it could be inferred that in the presence of Co, the addition of Cu was beneficial to improve synergistic catalytic activity, so the simultaneous participation of the two metal centers accelerates the production of the target products (Table 1, entry 1-5). As a comparison, the hydrogenation reaction using precious metals often required high-pressure hydrogen, and exhibited low conversion and low selectivity for the aldehyde reduction (Table 1, entry 6-7). Using single component of UiO-66 cannot completely convert nitrobenzaldehyde into corresponding alcohols but with by-products (conversion:79% and selectivity: 77%). Using $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu$ as the sole catalyst, the conversion and selectivity were 50% and 78%, respectively. When $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu$ was employed with UiO-66, the conversion and selectivity of nitrobenzaldehyde both reached 99%. In order to further improve the catalytic efficiency, we employed this armoured core-shell structure $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$, and it was found that the conversion and yield were greatly improved, both of which could attain 99% (Table 1, entry 8-10). However, in the method of in-situ synthesis, $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu$ and UiO-66 exist separately, so the catalytic system is not stable. When the physically mixed catalyst is recycled for 3 cycles, the catalytic performance begins to decrease (Table 1, entry 11) .

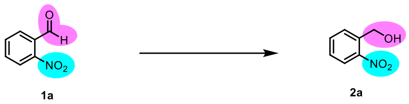
Table 1. Catalyst screening for the selective transfer hydrogenation of nitrobenzaldehyde.[a]



Entry	Catalyst	Conv. (%) [b]	Sel. (%) [c]
1	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}Co_3O_4$	40	55
2	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}FeNi$	trace	25
3	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}FeCu$	trace	36
4	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoNi$	27	20
5	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu$	50	78
6	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}Pd$	42	65
7	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}Rh$	38	62
8	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$	99	99
9[d]	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$	99	99
10	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu/UiO\text{-}66$	99	99
11[d]	$Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu/UiO\text{-}66$	73	99

[a] Reaction conditions: nitrobenzaldehyde **1a** (1 mmol), isopropanol (10 mL), catalyst (30 wt%), 110 °C. [b, c] Determined by GC. [d] Catalytic efficiency of catalyst after 3 cycles.

Table 2. Selective hydrogenation of nitrobenzaldehyde to nitrobenzyl alcohol in different reaction conditions.[a]



Entry	Tempera-ture (°C)	Solvent volume (mL)	Catalyst dosage (wt%)	Reation time (h)	Conv./sel. (%) [e]
1[b]	80	10	20	10	26/17
2[b]	110	10	20	10	34/49
3[b]	110	10	20	12	34/49
4[b]	110	10	30	12	40/55
5[c]	80	5	30	10	44/53
6[c]	100	5	30	10	76/81
7[c]	110	5	30	10	83/90
8[c]	110	10	30	10	89/97
9[c]	110	10	30	12	99/99
10[c, d]	110	10	30	12	99/99

[a] Reaction conditions: 1 mmol nitrobenzaldehyde **1a** (1 mmol), isopropanol (10 mL), catalyst. [b] Using $Fe_3O_4@SiO_2\text{-}NH_2\text{-}Co_3O_4$ as the catalyst. [c] Using $Fe_3O_4@SiO_2\text{-}NH_2\text{-}CoCu@UiO\text{-}66$ as the catalyst. [d] Without base. [e] Determined by GC.

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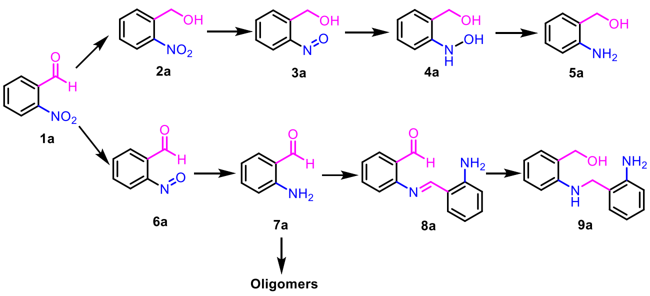
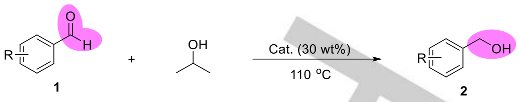
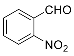
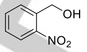
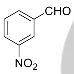
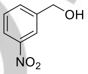
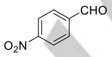
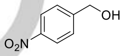
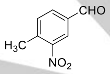
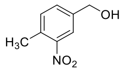
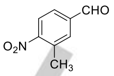
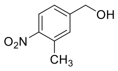
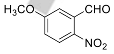
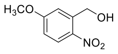
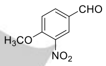
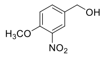
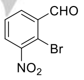
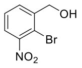
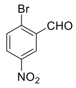
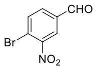
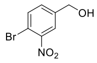
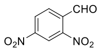
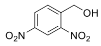
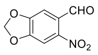
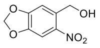
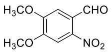
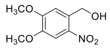
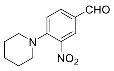
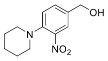
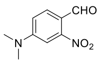
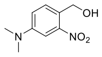


Scheme 2. Possible pathways and by-products in the selective transfer hydrogenation of nitrobenzaldehydes.

In the preliminary research process, we optimized the selective hydrogen transfer reaction conditions of 2-nitrobenzaldehyde (Table 2). The experimental results showed that increasing the amount of catalyst and prolonging the reaction time were beneficial to improve the conversion rate of the target product, and raising the reaction temperature could obtain a higher selectivity for carbonyls (Table 2, entry 1-2, 5-7). The energy released by the new bond was insufficient at lower temperatures, which could also lead to by-products (Scheme 2). Excessive hydrogenation of nitrobenzaldehyde may lead to the reduction of aldehyde groups to alcohols, and nitro groups will be partially hydrogenated or completely hydrogenated to amino groups. When only the nitro group was reduced to amino group, the generated primary amine may even undergo condensation reaction with the aldehyde to form imines **8a**, amines **9a** or even complex by-products of oligomers. Moreover, increasing the amount of catalyst was equivalent to increasing the active sites of the reaction, and long-term constant-temperature heating was conducive to the complete conversion of the reactant (Table 2, entry 2-4). In the subsequent study, the catalytic result of $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66 on the template reaction was consistent with the one of $Fe_3O_4@SiO_2$-NH_2-Co_3O_4 (Table 2, entry 5-10). It was worth noting that the encapsulated catalyst had rich acid sites and did not require the activation of isopropyl alcohol by base substances, saving energy and making the reaction process more environmentally friendly (Table 2, entry 10) With the identified catalyst in hand, we investigated the substrate scope of transfer hydrogenation with a variety of nitrobenzaldehydes. As shown in Table 3, the selectivity of all substrates could be more than 85%. The nitrobenzaldehydes with extra electron-withdrawing groups, such as bromine, nitro, showed excellent reactivity, whose corresponding alcohols were generated in 96-99% yields (Table 3, entries 8–11). In addition, reactions of nitrobenzaldehydes bearing one or two electron-donating substituents, such as methyl, methoxy, dimethoxy and heterocycle groups, afforded the desired products in 84-95% yields (Table 3, entries 4–7, 12–14). Among them, substrates with relatively large steric hindrance required a long reaction time to achieve a high conversion rate (Table 3, entries 12–15). More importantly, the stronger the electron withdrawing capacity or the greater the numbers of electrondrawing groups, the faster the reaction speed, and vice versa. Because the electron-withdrawing groups reduced the density of the electron cloud of C=O, and the induction effect and conjugation effect could facilitate the C=O bond break and accelerate the reaction.

Table 3. Various substrates of nitrobenzaldehydes for the selective transfer hydrogenation.[a]



Entry	Substrate	Time (h)	Product	Conv./sel. (%) [b]
1	 1a	12	 2a	99/99
2	 1b	12	 2b	96/94
3	 1c	12	 2c	99/98
4	 1d	12	 2d	88/95
5	 1e	12	 2e	90/94
6	 1f	12	 2f	86/87
7	 1g	12	 2g	85/88
8	 1h	12	 2h	98/98
9	 1i	12	 2i	98/98
10	 1j	12	 2j	96/97
11	 1k	11	 2k	99/98
12	 1l	14	 2l	95/98
13	 1m	13	 2m	84/87
14	 1n	15	 2n	90/96
15	 1o	13	 2o	20/92

[a] Reaction conditions: Nitrobenzaldehyde **1a** (1 mmol), catalyst (30 wt% of substrate) in 10 mL of isopropanol were heated at 110 °C. [b] Determined by GC.

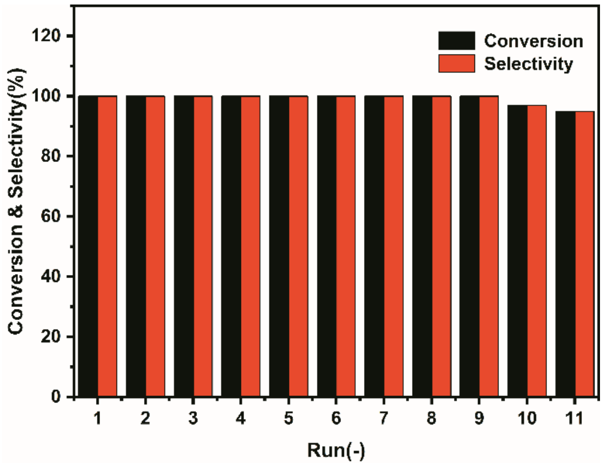
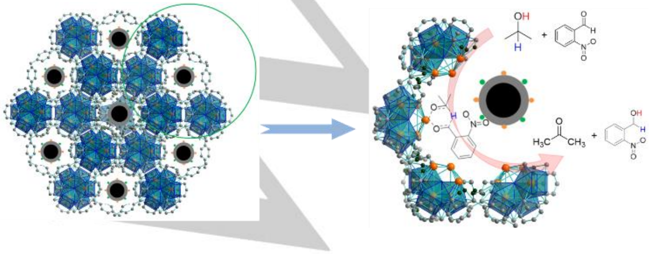


Figure 3. The conversions and selectivities of catalytic system $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66

The molecular sizes obtained by Gaussian software optimization of some substrate molecules were shown in Table S1. The lengths of the three sides of 4-dimethylamino-2-nitrobenzaldehyde are 1.21 nm, 0.91 nm and 0.50 nm (Figure S5). The structure of the MOF shell restricted reactants to contact CoCu sites, while UiO-66 alone could only give 20% yield of 4-dimethylamino-2-nitrobenzyl alcohol. 3-nitro-4-(1-pyrrolidine) benzaldehyde (the length of the three sides: 0.88 nm, 1.21 nm, 0.37 nm) had a similar electronic structure, which was not hindered by the MOF shell, and the conversion rate was as high as 90%, which further proved that CoCu nanoparticles were effective for catalyzing the carbonyl compounds in the hydrogen transfer reaction. In addition, the presence of MOF prolongs the service life of the catalyst. The stability of $Fe_3O_4@SiO_2$-NH_2-CoCu@UiO-66 was also tested (Figure 3), and the catalyst exhibited almost no activity change in the first nine runs, and the activity remained at 98% of the initial level after eleven runs. The excellent cycle stability of the catalyst has an indispensable relationship with the protection of MOF and great dispersion.

Based on the experimental results and related refereces,[22] the possible mechanism of this selective transfer hydrogenation of nitrobenzaldehydes with isopropanol was studied and proposed (Scheme 3). Initially, the oxygen atom of the carbonyl group in nitrobenzaldehyde preferentially coordinated with the Lewis acid metal atom Zr in the UiO-66 armour. Then, metal nanoparticles on the core could adsorb nitro groups, which probably played an role of protecting the nitro group, and Co nanoparticles tended to promote the production of hydrogen.[21] So in this catalytic system, the armour-core structure could offer an appropriate microenvironment, so-called selective gate, beneficial for the synergistic effect that is the double-sites interactiom with aldehyde and nitro groups. It was important that the hydrogenation strength of isopropanol alone would not achieve the selective reduction. More significantly, during the reaction, the Lewis acid site, isopropanol, and carbonyl group could probably form a six-membered ring transition state,[22] which was crucial for the further hydrogen transfer to the carbonyl group. The isopropanol anion would directly render the α-H to transfer to the carbonyl group in nitrobenzaldehyde to be oxidized to acetone.[23] At the same time, the aldehyde was reduced to an alkoxy anion, which underwent the proton transfer with isopropanol to produce the corresponding alcohols. The hydrogen transfer process was similar to the Meerwein-Ponndorf-Verley (MPV) reaction mechanism. We employed FT-IR spectroscopy and nuclear magnetic resonance (NMR) technique to study the mechanism in order to verify the interaction between the catalytic sites and 2-nitrobenzaldehyde in isopropanol system during the reaction. In the FT-IR spectroscopy (Figure 4a), we can observe that the asymmetric stretching vibration peak and the symmetric stretching vibration peak of NO_2 at 1521 cm^{-1} and 1346 cm^{-1} shift to 1535 cm^{-1} and 1356 cm^{-1}, respectively, and this blue shift can result from the interaction between NO_2 group and CoCu sites, while there is no change for the infrared absorption of C=O group at 1698 cm^{-1}, implying that $Fe_3O_4@SiO_2$-NH_2-CoCu only reacts with nitro groups, and does not interact with carbonyl groups in 2-nitrobenzaldehyde. In addition, the effect of Zr site on the carbonyl group was verified by ^1H NMR spectrum of the 2-nitrobenzaldehyde and $ZrCl_4$ mixture, and the carbonyl signal can be observed to shift from 10.4 to 10.3 ppm also with the peak splitting at 10.3 ppm, which illustrated the interaction between Zr site and C=O (Figure 4b). Subsequently, 2-nitrobenzaldehyde, $ZrCl_4$ and isopropanol were mixed to stimulate the reaction system, whose ^1H NMR spectrum also showed the evidence for the interaction between the three components. It can be observed that the hydrogen signal on the tertiary carbon in isopropanol shows a large shift from 3.58 to 3.29 ppm towards high field, this shift may be induced both by Zr site and aldehyde group (Figure 4c). At the same time, the C=O signal also has a significant shift, probably being influenced by both isopropanol and Zr site (Figure 4d). All these evidences



Scheme 3. Plausible reaction mechanism for selective transfer hydrogenation of 2-nitrobenzaldehyde.

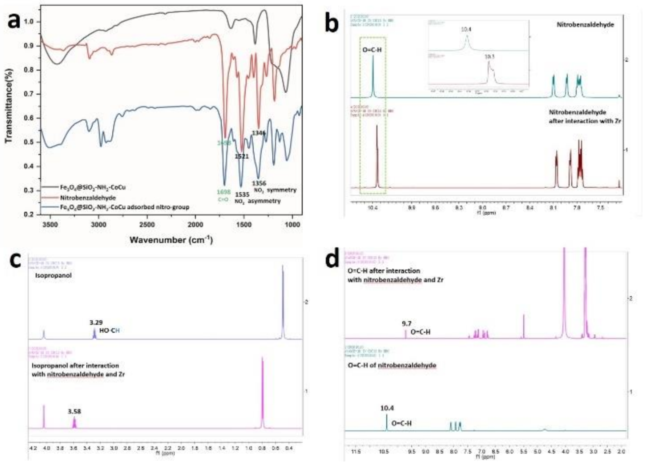


Figure 4. The mechanism investigation by FT-IR spectra and ^1H NMR technique (400 MHz, $CDCl_3$). a) The FT-IR spectra of the mixed system of $Fe_3O_4@SiO_2$-NH_2-CoCu and 2-nitrobenzaldehyde. b) ^1H NMR spectrum of the 2-nitrobenzaldehyde and $ZrCl_4$ mixture. c), d) The ^1H NMR spectrum of three-component system involving 2-nitrobenzaldehyde, $ZrCl_4$, and isopropanol.

would conform to the proposed six-membered ring transition state during our selective transfer hydrogenation according to experimental verification and literature exploration.[24]

Conclusion

In summary, we have successfully designed and synthesized an armour-type composite catalyst of metal organic framework-capsulated magnetic CoCu nanoparticles ($Fe_3O_4@SiO_2-NH_2-CoCu@UiO-66$) by the novel half-way injection method for the selective transfer hydrogenation. Remarkably, a part of nitrobenzaldehydes can be selectively hydrogenated into corresponding nitrobenzyl alcohols in extremely high conversion (99%) and selectivity (99%) rather than the hydrogenation of nitro group. Probably, the acid sites of the catalyst could preferentially bind with the carbonyl group and form a crucial six-membered ring transition state with isopropanol, and metal nanoparticles could adsorb and preserve the nitro group. In addition, this armoured catalyst can be recycled under the same conditions for 9 cycles without the loss of activity. The armoured UiO-66 armour can serve as the active component for this catalytic reaction, not only stabilize CoCu nanoparticles, improve the recycling of the catalyst, but also cooperate with metal nanoparticles to accelerate the hydrogen transfer reaction rate, which achieves this synergistically catalytic and controllable reaction in a “1+1>2” manner.

Experimental Section

Preparation of $Fe_3O_4@SiO_2-NH_2$: Typically, Fe_3O_4 (0.2 g) was dispersed and activated with 50 mL HCl solution (0.125 mol/L). After ultrasonic treatment for 20 min, pre-treated activated Fe_3O_4 was dispersed in the mixture containing ethanol (170 mL) water (30 mL) and ammonium hydroxide (4 mL, 25%). Tetraethyl orthosilicate (TEOS, 1 mL) was injected slowly into the solution with continuous vigorously stirring for 5 hours. Next, the solid components were separated by magnetic collection in the above steps and re-dispersed in isopropanol (180 mL) containing APTES (0.5 mL) at 90 ºC for 3 hours in order to synthesize $Fe_3O_4@SiO_2-NH_2$. At last, the product was gathered by the magnet and washed with ethanol for three times.

Preparation of $Fe_3O_4@SiO_2-NH_2-CoCu$ NPs: $Fe_3O_4@SiO_2-NH_2$ (100 mg), $Co(NO_3)_2{\cdot}6H_2O$ (0.2 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.2 mmol) were dissolved in methanol (100 mL) under the protection of Ar with continued stirring for 1 hour. Next, $NaBH_4$ (0.4 g) was dissolved in 10 mL methanol solution and injected into the reaction mixture at room temperature and stirred for 8 hours. Finally, the black solid was separated by the magnet and washed for three times with ethanol.

Preparation of $Fe_3O_4@SiO_2-NH_2-CoCu@UiO-66$: Equal molar amounts of $ZrCl_4$ and 1, 4-benzenedicarboxylate (H_2BDC) were dissolved in 100 mL DMF solution. Then, acetic acid (10 mL) was added in the mixture with vigorously stirring. During the budding period of UiO-66 growth, $Fe_3O_4@SiO_2-NH_2-CoCu$ was injected into MOF precursors solution. The final UiO-66-capsulated was washed with ethanol for three times.

Catalytic transfer hydrogenation reaction of nitroaldehydes: Nitroaldehydes (1 mmol) and catalyst (30 wt%) were mixed into a sealed tube. The isopropanol (10 mL) was added as solvent and hydrogen source. The reaction was carried out at 110 ºC and the conversions and yields were monitored by GC. After the separation, the catalyst was reused without extra treatment after washing under the same condition.

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Keywords: MOF-capsulated composite • Half-way Injection Method • Selective transfer hydrogenation • Metal nanoparticles • Nitrobenzaldehydes

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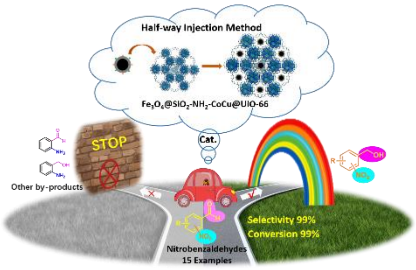

1. An armour-type composite of metal organic framework-capsulated CoCu nanoparticles with Fe_3O_4 core was designed and synthesized by a novel half-way injection method.

2. Fe_3O_4@SiO_2-NH_2-CoCu@UiO-66 serves as an efficient and recyclable catalyst for the selective transfer hydrogenation of nitrobenzaldehydes in high selectivity (99%).

3. This novel method and ingenious combination of MOF and nanoparticles implements a “1+1>2” strategy in catalysis.

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