



Co-MOF-74@Cu-MOF-74 Derived Bifunctional Co-C@Cu-C for One-Pot Production of 1, 4-Diphenyl-1, 3-Butadiene from Phenylacetylene

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Abstract: Carbon supported metal nanoparticles (NPs) play important roles in heterogeneous catalysis. In particular, supported bimetallic catalytic systems can be promising multifunctional catalysts for one-pot tandem/cascade reactions, in which two or more successive independent reactions are realized in one pot. In this manuscript, we reported the preparation of a carbon-supported bimetallic CoCu catalytic system (Co-C@Cu-C), with Co NPs wrapped by carbon supported Cu NPs, from the pyrolysis of a coreshell structured Co-MOF-74@Cu-MOF-74. The as-obtained Co-C@Cu-C acts as a bifunctional catalyst for the transformation of phenylacetylene to 1, 4-diphenyl-1, 3-butadiene in one pot, in which supported metallic Cu NPs and Co NPs are active for the coupling and hydrogenation reaction respectively. By tuning the reaction rates of the coupling and the hydrogenation in this tandem reaction over the Co-C@Cu-C via changing the reaction medium and the reducing agent, an efficient direct transformation of phenylacetylene to 1, 4diphenyl-1, 3-butadiene was realized. This work not only highlights the important role of MOFs in the preparation of multifunctional carbon supported metal NPs for heterogeneous catalysis, but also demonstrates the possibility of tuning the reaction rates of different catalytic steps in a tandem reaction to realize an efficient overall reaction.

Introduction

Metal nanoparticles (NPs) play important roles in heterogeneous catalysis.^[1] Catalytic active metal NPs are usually loaded on different supports for their applications in heterogeneous catalysis, not only to reduce the amount of their usage but also to improve their stability during the reactions since the metal NPs have high surface energy and are prone to sintering at high temperature.^[2] Due to the high surface area and excellent thermal and mechanical properties, different allotropes of carbon have been used as supports for catalytic active metal NPs.^[3] In addition, the carbon support can also endow the catalysts with additional adsorption sites for the reactants.^[4] An efficient strategy to obtain

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carbon supported metal NPs with regular size and their even dispersion on the supports is the pyrolysis of the metal containing inorganic-organic polymeric complexes.^[5] In particular, metalorganic frameworks (MOFs), a class of porous inorganic-organic hybrid materials, have been found to be an extremely appealing type of precursors for fabricating various carbon supported metal NPs, which have been applied in many fields.^[6] Since the metal cations in the MOFs are reduced by the in-situ generated carbon matrix from the decomposition of the organic ligands, strong interactions between the metal NPs and the carbon support exist in the thus-obtained carbon supported metal NPs. In addition, the advantages of using MOFs as a precursor lies in that isolated and uniform distributed metal NPs in the carbon support can be obtained due to the regular arrangement of the metal cations and the organic components within the crystalline MOF structures.^[7]

Recently, with an aim of developing green and atomeconomic catalytic processes, researchers are paying increasing attention to the tandem/cascade reactions, in which two or more successive independent reactions are realized in one pot. As compared with traditional catalysis, one-pot tandem/cascade reactions offer enormous economic advantages since the separation of the reaction intermediates can be avoided, and therefore can save the processing time and minimize the waste production.^[8] In contrast to the traditional one-catalyst/onereaction approach, multifunctional catalyst, which contains different spatially separated catalytic active sites to maintain their independent function, is usually required for the one pot tandem/cascade reaction.^[9] Bimetallic catalytic systems, if well designed and fabricated, can be promising multifunctional catalysts for one-pot tandem/cascade reactions since metalbased catalytic activities in these systems can be combined and cooperated. However, synchronizing the reaction rates of the different catalytic steps in a tandem/cascade reaction to realize an efficient overall reaction, which theoretically can be realized via a delicate tuning of the bimetallic catalytic system, is still a great challenge. [10]

M-MOF-74 (M = divalent cations) is a MOF material constructed from divalent cations and 2, 5-dihydroxyterephthalic acid (H₄DOBDC).^[11] Our previous study revealed that Cu-MOF-74 derived carbon supported Cu-based catalyst can activate terminal alkynes to form the copper(I) acetylides and as a result, can catalyze the C-C coupling of the terminal alkynes.^[12] In addition, Co-MOF-74 derived carbon coated metallic Co NPs acted as an excellent catalyst for selective semi-hydrogenation of aromatic alkynes to alkenes with NaBH₄.^[13] Therefore, in this manuscript, we rationally combined these two catalysts to afford a carbon-supported bimetallic CoCu catalytic system, with Co NPs wrapped by carbon supported Cu NPs (Co-C@Cu-C), from

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the pyrolysis of a core-shell structured Co-MOF-74@Cu-MOF-74. The as-obtained Co-C@Cu-C acts as a bi-functional catalyst for the one pot tandem reaction to transform phenylacetylene to 1, 4-diphenyl-1, 3-butadiene, in which supported metallic Cu NPs and Co NPs are active for the coupling and hydrogenation reaction respectively. By tuning the reaction rates of the coupling and the hydrogenation in this tandem reaction over the Co-C@Cu-C via changing the reaction medium and the reducing agent, an efficient direct transformation of phenylacetylene to 1, 4-diphenyl-1, 3-butadiene was realized. This work not only highlights the important role of MOFs in the preparation of multifunctional carbon supported metal NPs for fheterogeneous catalysis, but also demonstrates the possibility of tuning the reaction rates of different catalytic steps in a tandem reaction to realize an efficient overall reaction.

Results and Discussion

was The core-shell structured Co-MOF-74@Cu-MOF-74 fabricated by a two-step microwave method. First, Co-MOF-74 was synthesized via a modified microwave-assisted method from Co(NO₃)₂·6H₂O and H₄DOBDC, with its XRD shown in Figure 1a (Step 1 in Scheme 1). To prepare Co-MOF-74@Cu-MOF-74, Cu(CH₃COO)₂ and H₄DOBDC was introduced into a DMF solution containing the preformed Co-MOF-74 and the resultant suspension was heated with the assistance of microwave at 130 °C. The XRD pattern of the as-obtained Co-MOF-74@Cu-MOF-74 correlated well with that of Co-MOF-74 (Figure 1a), indicating that the framework of MOF-74 was retained after the introduction of Cu. The TEM image shows that the morphology of the as-obtained Co-MOF-74@Cu-MOF-74 is rod-shaped, with a diameter of ca. 100 nm and a length of ca. 650 nm (Figure 1b). The HADDF-STEM image (Figure 1c), with the EDX line-scan along the cross section (inset in Figure 1c), revealed a clear boundary between Co and Cu segment. It is therefore proposed that Cu2+ ion coordinated with H4DOBDC on the surface of the Co-MOF-74 and led to a layer by layer growth of Cu-MOF-74 on

the surface of Co-MOF-74 to form the core-shell structured Co-MOF-74@Cu-MOF-74, as shown in Scheme 1 (Step 2). The ICP-OES analysis revealed that the amount of Co and Cu in Co-MOF-74@Cu-MOF-74 was 9.87% and 27.06% respectively, with a Co/Cu ratio to be 0.36.

Although the pyrolysis of M-MOF-74 to obtain different carbon supported metal NPs have been demonstrated, the products obtained via calcinating the MOFs depend not only on the metal ions in the MOFs, but also on the calcination conditions.^[14] To obtain carbon supported metallic Co and Cu from Co-MOF-74@Cu-MOF-74, TGA was carried out over Co-MOF-74@Cu-MOF-74 to provide guidance for its pyrolysis. The TGA result showed three apparent weight loss regions in 50-210, 210-560 and 560-1100 °C (Supporting Fig. S1). The weight loss at 210-560 °C can be attributed to the decomposition of the organic ligands. Different from Co-MOF-74, Co-MOF-74@Cu-MOF-74 has a faster weight loss rate at the second region, which may be caused by the decomposition of the outer shell of Cu-MOF-74 with lower crystallinity. The weight loss region at 560-1100 °C can be attributed to the reduction of Cu²⁺ and Co²⁺ to form metallic Cu and Co NPs, which was similar to our previous work.

Therefore, to obtain carbon supported metallic Co and Cu NPs, Co-MOF-74@Cu-MOF-74 was calcinated at 1000 °C (Step 3 in Scheme 1). The XRD patterns of the product obtained from Co-MOF-74@Cu-MOF-74 shows six peaks at 43.4°, 44.1°, 50.3°, 51.6°, 74.1° and 75.9° (Figure 2a). The peaks at 44.1°, 51.6° and 75.9° are corresponding to (111), (200) and (220) crystallographic planes of cubic Co (JCPDS 01-089-7093), while the other three peaks at 43.4°, 50.3° and 74.1° can be indexed to (111), (200) and (220) crystallographic planes of cubic Cu (JCPDS 01-070-3038), respectively. Besides the peaks attributable to metallic Co and Cu, a broad yet weak diffraction peak at 24.6° assignable to graphitic carbon is also observed. The XRD result clearly indicated that the pyrolysis of Co-MOF-74@Cu-MOF-74 at 1000 °C led to the formation of graphitic carbon supported metallic Cu and Co NPs (denoted as Co-C@Cu-C). Accordingly, the FT-IR spectrum of Co-C@Cu-C showed that the intensity of the peaks in the region from 1000 cm⁻¹ to 1600 cm⁻¹ observed in the



Figure 1. Co-MOF-74@Cu-MOF-74 (a) XRD; (b) TEM image; (c) HAADF-STEM image and EDX line-scan of the enlarged area (inset).

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Figure 2. Co-C@Cu-C (a) XRD patterns; (b) TEM and HRTEM images; XPS spectrum in (c) Co region and (d) Cu region.

original Co-MOF-74@Cu-MOF-74 dramatically decreases, confirming the successful decomposition of organic framework during the calcination (Supporting Fig. S2).

The TEM image of the as-obtained Co-C@Cu-C shows rod with a diameter of ca. 100 nm, indicating that the morphology of the Co-MOF-74@Cu-MOF-74 was maintained after the pyrolysis (inset in Figure 2b). However, unlike Co-MOF-74@Cu-MOF-74 which has a smooth surface, the TEM image of Co-C@Cu-C clearly shows that its surface is rough, with spherical nanoparticles of ca. 3-4 nm evenly distributed on the outside of the rod (Figure 2b). These nanoparticles are confirmed to be metallic Cu NPs since lattice fringes of d = 0.208 nm, which matches well with (111) crystallographic plane of cubic Cu, are observed in the HRTEM image (inset in Figure 2b). Apart from Cu NPs, lattice fringes of d = 0.204 nm, attributed to cubic Co, can also be observed (inset in Figure 2b). As compared with metallic Cu NPs, the size of metallic Co NPs is much bigger, which shows a diameter of ca. 18 nm. The TEM image also confirms that Co NPs are enwrapped by supported Cu NPs. Since metallic Cu and Co NPs were formed via the reduction of cationic metal ions in the MOFs by the in-situ produced carbon, the regular arrangement of the metals and the organic components in MOF-74 led to a uniform distribution of the metal NPs on the carbon matrix.

Table 1. The conversion of phenylacetylene over Co-C@Cu-C and other catalysts under different conditions.

Entry	Solvent	Catalyst	Reducing agent	Conv. (%)	Selectivity (%)			
					Ar	Ar	Ar	Ar
1	THF	Co-C@Cu-C	NaBH4	13	25	_[a]	51	24
2	CH ₂ Cl ₂	Co-C@Cu-C	NaBH4	2	-	-	>99	-
3	EtOH	Co-C@Cu-C	NaBH4	>99	80	12	5	-
4	i-PrOH	Co-C@Cu-C	NaBH4	>99	54	39	7	-
5	THF:i-PrOH=3:1	Co-C@Cu-C	NaBH4	87	52	-	4	41
6	THF:i-PrOH=3:1	Co-C@Cu-C	-	52	-	-	>99	-
7	THF:i-PrOH=3:1	Co-C	NaBH4	95	98	-	-	-
8	THF:i-PrOH=3:1	Cu-C	NaBH4	74	3	-	95	-
9 ^[b]	THF:i-PrOH=3:1	Co-C@Cu-C	NaBH4	-	-	-	-	-
10 ^[c]	THF:i-PrOH=3:1	Co-C@Cu-C	NaBH4	-	-	-	-	-
11	THF:i-PrOH=3:1	Co-C@Cu-C	NH3BH3	77	24	-	13	63
12 ^[d]	THF:i-PrOH=3:1	Co-C@Cu-C	NH3BH3	>99	28	3	12	57
13	THF:i-PrOH=3:1	Co-Cu-C	NH ₃ BH ₃	56	37	25	21	13
14	THF:i-PrOH=3:1	Co-C&Cu-C	NH3BH3	93	74	-	8	16
15	THF:i-PrOH=3:1	Cu-C@Co-C	NH3BH3	>99	65	9	22	3
16 ^[e]	THF:i-PrOH=3:1	Co-C@Cu-C	NH3BH3	75	25	-	14	61

Reaction conditions: catalyst (5 mg), solvent (4 ml) and phenylacetylene (5.5 µL, 0.05 mmol), reducing agent (0.05 mmol), K₂CO₃ (20 mg), 323 K, 10 h. [a] "-" refers to no products were detected. [b] styrene as substrate. [c] 1, 4-diphenylbutadiyne as substrate. [d] 13 h. [e] recycle stability test.

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In consistence with the results from the XRD and TEM results, the XPS of Co-C@Cu-C shows two wide peaks in Co 2p region, which can be deconvoluted into two sets of peaks (Figure 2c). The peaks with binding energy at 779.66 eV and 795.13 eV can be attributed to $2p_{3/2}$ and $2p_{1/2}$ of metallic Co⁰, while the other two small peaks at 781.88 eV and 797.10 eV can be assigned to those from Co2+. Since no diffraction peaks corresponding to CoO was observed in the XRD pattern of Co-C@Cu-C, the presence of Co2+ is probably ascribed to the partial oxidation of the surface of metallic Co. The XPS of Co-C@Cu-C in the Cu region shows two peaks with binding energy at 932.36 eV (2p_{3/2}) and 952.22 eV (2p_{1/2}), corresponding to Cu⁰ (Figure 2d). In addition to these, two small peaks at 934.10 eV and 954.10 eV are also observed, indicating the coexistence of Cu2+, probably ascribed to the partial oxidation of the surface of Cu NPs. The amount of Co and Cu in Co-C@Cu-C was determined to be 11.52% and 30.12%, with a Co/Cu ratio (0.38) comparable to that in Co-MOF-74@Cu-MOF-74 (0.36). Therefore, morphology-maintained transformation of rod-shape Co-MOF-74@Cu-MOF-74 to carbon supported Co and Cu NPs has been successfully realized by pyrolysis of Co-MOF-74@Cu-MOF-74 at 1000 °C.

The catalytic performance of the as-obtained Co-C@Cu-C for the transformation of phenylacetylene to 1, 4-diphenyl-1, 3butadiene was first investigated in THF using NaBH₄ as the reducing agent. As shown in entry 1 (Table 1), 13% of phenylacetylene was converted, with a selectivity of only 24% to 1. 4-diphenvl-1. 3-butadiene after 10 h. In addition, a selectivity of 51% to 1, 4-diphenylbutadiyne was also detected. This indicated that although one pot transformation of phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene was possible, the performance over the current system was still too low due to the existence of the side reactions. To investigate the possibility of tuning the rates of the coupling and the hydrogenation by changing the reaction medium, the reactions were carried out in different solvents. The performance of the reaction was influenced by the reaction medium. For example, when aprotic solvents like CH₂Cl₂ was used, the main product was 1, 4diphenylbutadiyne (Table 1, entry 2), while hydrogenated product like styrene and ethylbenzene were mainly obtained when protonic solvents such as EtOH or i-PrOH was used as the solvent (Table 1, entry 3 and 4). The above results clearly indicated that proton solvents can facilitate the hydrogenation reaction, probably due to its higher capability for proton transfer. Among the solvents investigated, a mixed solvent containing THF/i-PrOH (v/v =3:1) gave the best performance by showing the highest phenylacetylene conversion ratio of 87%, with a selectivity of 41% to 1, 4-diphenyl-1, 3-butadiene (Table 1, entry 5). Only 1, 4diphenylbutadiyne was detected when the reaction was carried out in absence of NaBH₄ under otherwise similar conditions, indicating that the formation of 1, 4-diphenyl-1, 3-butadiene is truly promoted by Co-C@Cu-C through the transfer hydrogenation (Table 1, entry 6). When Co-MOF-74 derived Co-C was used as the catalyst, only styrene, the hydrogenation product was detected, indicating that the hydrogenation occurs over metallic Co NPs (Table 1, entry 7). On the contrary, only 1, 4diphenylbutadiyne, the coupling product, was obtained over Cu-MOF-74 derived Cu-C, suggesting that metallic Cu is involved in the coupling of phenylacetylene (Table 1, entry 8).

The above results were consistent with previous studies, which showed that Cu-based catalyst can catalyze the C-C coupling of the terminal alkynes, while the dissocciation of BH_4^-

occurs over Co NPs to generate H⁻ for the hydrogenation of alkynes.^[15] It is therefore proposed that over the as-obtained Co-C@Cu-C, the conversion of phenylacetylene to 1, 4-diphenyl-1, 3-butadiene has undergone a tandem hydrogenation and C-C coupling, as shown in Scheme 2. The first step in this process is the activation of phenylacetylene by metallic Cu NPs. Due to a lower work function of Cu (4.65 eV) compared to carbon (4.81 eV) as well as the existence of the strong interactions between the carbon support and metallic Cu, electrons transfer from metallic Cu to carbon matrix when heated and Cu⁺-phenylacetylide complex was formed on the surface of Cu NPs (step 1 in Scheme 2).^[16] The involvement of the formation of Cu⁺-phenylacetylide complex in the first step was confirmed by the result obtained from the controlled experiment carried out using styrene as the substrate, which shows almost no 1, 4-diphenyl-1, 3-butadiene was obtained (Table 1, entry 9). In the meantime, the dissociation of NaBH₄ occurs on the surface of metallic Co NPs in Co-C@Cu-C to form Co-BH₃ and Co-H, which acts as the active species for the hydrogenation of phenylacetylene (step 2 in Scheme 2). The hydrides on Co NPs can spillover to Cu NPs through carbon matrix, and react with the adsorbed Cu⁺-phenylacetylide complex to form complex (A) (step 3 and 4 in Scheme 2). The spillover of the hydrides from the metal NPs to the carbon materials has already been demonstrated.^[17] The hydrogenation of 1, 4diphenylbutadiyne over Co-C@Cu-C showed that no target product was formed (Table 1, entry 10). The participation of isopropanol in this reaction was confirmed since almost no hydrogenation products were detected when isopropanol was replaced by CH₂Cl₂ (Table 1, entry 2). The remaining hydrides in BH₃(i-PrO)⁻ can also be dissociated sequentially over metallic Co NPs, and spillover through the carbon matrix to react with the adsorbed Cu⁺-phenylacetylide complex to form anothor complex (A), with BH₂(i-PrO)⁻ left in the reaction system (steps 5 in Scheme 2). The in-situ formed complex (A) can dimerize to form 1, 4diphenyl-1, 3-butadiene (steps 6 in Scheme 2). Surely, side reactions including the direct hydrogenation of phenylacetylene to produce styrene and the direct dimerization of Cu+phenylacetylide complex to form 1, 4-diphenylbutadiyne also exist. Therefore, suppressing the side reactions is important for improving the selectivity to the target 1, 4-diphenyl-1, 3-butadiene in this tandem reaction.



Scheme 2. Proposed mechanism for the one pot tandem reaction of phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene over Co-C@Cu-C using NaBH₄ as the reducing agent.

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The regulation of the kinetics of the hydrogenation and the C-C coupling is important to ensure an efficient formation of 1, 4diphenyl-1, 3-butadiene. Since the reaction over Co-C@Cu-C using NaBH₄ as the reducing agent gave a high selectivity of 52% to styrene, the byproduct due to the side reaction of the direct hydrogenation of phenylacetylene, it is anticipated that the using of NH₃BH₃, a milder reducing agent than NaBH₄, would decrease the rate of the hydrogenation and optimize the desired reaction to yield 1, 4-diphenyl-1, 3-butadiene. Therefore, the reaction using NH₃BH₃ as the reducing agent was investigated under otherwise conditions. As expected, the reaction between NH3BH3 and phenylacetylene over Co-C@Cu-C gave 1, 4-diphenyl-1, 3butadiene as the main product, with a conversion of phenylacetylene to be 77% and a selectivity of 63% to desired 1, 4-diphenyl-1, 3-butadiene after 10 h, confirming that the wellmatched reaction kinetics resulted in a superior performance for tandem hydrogenation/coupling of phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene (Table 1, entry 11). An almost total conversion of phenylacetylene was achieved after reacting for 13 h, at the expense of a slightly decreased selectivity to 1, 4diphenyl-1, 3-butadiene (57%). (Table 1, entry 12). The reaction can also be applied to different phenylacetylene derivatives to produce corresponding diphenyl-1, 3-butadienes, although with varied activities (Supporting Table S1).



Figure 3. Co-Cu-C (a) XRD patterns; (b) TEM and (c, d) HRTEM images.

The above observations clearly demonstrated that Co-C@Cu-C derived from a well-designed core-shell structured Co-MOF-74@Cu-MOF-74 can act as a successful bi-functional catalyst for one pot transformation of phenylacetylene to 1, 4diphenyl-1, 3-butadiene via tandem hydrogenation/coupling. To demonstrate the effect of the structure of the precursor on the performance of the derived catalyst, Co-Cu-MOF-74, a bimetallic Co-Cu-based MOF-74 (denoted as Co-Cu-MOF-74), fabricated similarly to Co-MOF-74 by reacting $Cu(CH_3COO)_2$ Co(NO₃)₂·6H₂O and H₄DOBDC in one-pot, was used as the precursor to obtain carbon supported bimetallic Co-Cu catalyst (denoted as Co-Cu-C, Supporting Scheme S1). The formation of MOF-74 framework was evidenced from the XRD pattern of Co-Cu-MOF-74 (Supporting Figure S3a). The pyrolysis of Co-Cu-MOF-74 led to the formation of Co-Cu-C (Figure 3a, Supporting Fig. S3b) Unlike that in Co-C@Cu-C, the TEM image of Co-Cu-C shows that metallic Cu and Co NPs are randomly distributed on the carbon matrix (Figure 3b-d). The reaction carried out over Co-Cu-C under otherwise similar conditions revealed that 56% of phenylacetylene was converted, with a selectivity of only 13% to 1, 4-diphenyl-1, 3-butadiene (Table 1, entry 13). By-products including styrene and ethylbenzene (62%), the hydrogenation products, as well as 1, 4-diphenylbutadiyne (21%), the coupling product, were also detected. In addition, the pyrolysis of a

mechanical mixture of Cu-MOF-74 and Co-MOF-74 led to Co-C&Cu-C, which was also used for the reaction. Although 93% of phenylacetylene was converted after 10 h, the main product obtained was styrene, with a selectivity of only 16% to the desirable 1, 4-diphenyl-1, 3-butadiene (Table 1, entry 14). The poor performance observed over both Co-Cu-C and Co-C&Cu-C clearly highlights the important role of the core-shell structure of Co-MOF-74@Cu-MOF-74 to the catalytic performance of the derived bi-metallic catalytic systems. Cu-MOF-74@Co-MOF-74, with Cu-MOF-74 as a core and Co-MOF-74 as the shell, was also prepared via a similar strategy, which upon pyrolysis gave Cu-C@Co-C. Although phenylacetylene was also totally converted over Cu-C@Co-C after reacted for 10h, the main product obtained was styrene (65%), with a selectivity of only 3% to the desirable 1, 4-diphenyl-1, 3-butadiene (Table 1, entry 15). The exposure of the Co NPs to the substrate would make the rate of the hydrogenation too fast as compared with that of the coupling and resulted in the formation of more hydrogenated byproducts. The cover of metallic Co NPs with Cu NPs with a higher chemical stability not only helps to inhibit the oxidation of Co NPs, but also plays a vital role in regulating the reaction rate in a tandem reaction.

Co-C@Cu-C derived from Co-MOF-74@Cu-MOF-74 also showed high stability during the one pot transformation of phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene, which is highly important for its practical application. A cycling reaction revealed that no obvious loss of the activity, with 75% of phenylacetylene converted and a selectivity of 61% to 1, 4diphenyl-1, 3-butadiene (Table 1, entry 16). In addition, the recovered catalyst shows almost unchanged XRD and TEM image (Supporting Figure S4a and 4b)

Conclusion

In summary, supported Co NPs wrapped by carbon supported Cu NPs (Co-C@Cu-C) was successfully obtained from the pyrolysis of a core-shell structured Co-MOF-74@Cu-MOF-74, which acted as a bi-functional catalyst for the one pot tandem reaction to transform phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene. By changing the reaction medium and reducing agent, an optimized performance which show a phenylacetylene conversion of 77% and a selectivity of 63% to 1, 4-diphenyl-1, 3-butadiene was realized over Co-C@Cu-C when NH₃BH₃ was used as a reducing agent in THF/i-PrOH (v/v =3:1). This work highlights the important role of MOFs for the preparations of multifunctional carbon supported metal NPs for heterogeneous catalysis.

Experimental Section

Syntheses

MOFs precursors. M-MOF-74 (M = Co and Cu) were synthesized based on previously reported procedures.^[18] Co-MOF-74@Cu-MOF-74 was obtained by reacting Cu(CH₃COO)₂ and H₄DHBDC under microwave heating in the presence of pre-obtained Co-MOF-74. Co-Cu-MOF-74 was synthesized similarly to Co-MOF-74, except that equimolar of Cu(CH₃COO)₂ and Co(NO₃)₂·6H₂O was used as the metal precursors.

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MOF-derived carbon supported metal NPs. Co-C@Cu-C was prepared by the pyrolysis of Co-MOF-74@Cu-MOF-74 at 1000 °C similar to our previous work. Typically, the activated Co-MOF-74@Cu-MOF-74 was transferred into a ceramic boat and placed in a temperature-programmed furnace under a nitrogen flow. After that, Co-MOF-74@Cu-MOF-74 was heated slowly at a rate of 2 °C/min to 1000 °C and kept for 1 h. The product was collected after cooling to room temperature.

For comparison, Co-C, Cu-C and Co-Cu-C were obtained by pyrolysis of Co-MOF-74, Cu-MOF-74 and Co-Cu-MOF-74, respectively, following a similar procedure to that of Co-C@Cu-C.

Catalytic reactions

The reactions were carried out in a 10 ml quartz schlenk tube. Catalyst (5 mg) was treated under vacuum at 200 °C to remove any adsorbed species and purged with N₂. After NaBH₄ (2 mg, 0.05 mmol) and K₂CO₃ (20 mg) was added, ethanol (4 mL) and alkynes (5.5 μ L, 0.05 mmol), pre-degassed by N₂ to remove any dissolved O₂, was injected into the reaction tube. The reaction was carried out at 60 °C under N₂. After reaction, the mixture was filtered through a porous membrane (20 μ m in diameter) and the products were determined by GC (Shimadzu GC-2014), equipped with a flame ionization detector using a HP-5 capillary column, and an Agilent 7890B Series Gas Chromatograph (GC) linked to an Agilent 5977B Mass Selective Detector (MSD) was used in the analysis, allowing detailed information of the composition of the samples analysed to be obtained. The catalyst was recovered by centrifugation after reaction, and dried at 60 °C for cycle test.

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FULL PAPER

Entry for the Table of Contents



Bimetallic CoCu catalytic system (Co-C@Cu-C), with Co NPs wrapped by carbon supported Cu NPs, were obtained by pyrolysis of a core-shell structured Co-MOF-74@Cu-MOF-74, which shows an efficient one pot transformation of phenylacetylene to produce 1, 4-diphenyl-1, 3-butadiene, due to the synergistic roles played by supported metallic Cu NPs and Co NPs.