

Study of CoCu Alloy Nanoparticles Supported on MOF-Derived Carbon for Hydrosilylation of Ketones

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Abstract

Carbonized zeolitic imidazolate frameworks (ZIFs) show potential as mesoporous heterogeneous catalysts with high metal loadings. ZIF-67 and ZIF-8 were used to create mono- and bimetallic CoCu particles supported on nitrogen-doped carbon via self-assembly in methanol at room temperature, followed by carbonization at 675 °C. A Cu precursor, Cu(NO₃)₂·2H₂O, was impregnated into the ZIF-67 before carbonization to obtain bimetallic catalysts. Nanoalloy particles with different CoCu ratio were synthesized and characterized using XRD. The materials were further characterized using TEM, SEM, XRF and nitrogen physisorption. The different alloys were tested in conversion of cyclohexanone to the corresponding silyl ether. Complete conversion of cyclohexanone at 90 °C for 24 h were obtained. The catalyst Co₉₉Cu₁@NC gave a 60% increase in yield over a pure Co analogue.

Graphic Abstract



Keywords Hydrosilylation · MOF · ZIF-67 · Carbonization · Bimetallic alloy

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1 Introduction

The synthesis of new heterogeneous catalysts containing earth-abundant metals offers a way to create cheaper, more sustainable alternatives to more traditional catalysts containing precious metals like Pd, Pt or Ru [1–5]. One of the challenges of using earth-abundant metals is that they usually have much lower activities compared to their precious metal counterparts. This can often be circumvented by creating base metal nanoalloys [6–11]. According to Sabatier's Principle, there is an optimal adsorption energy between the reactant and the active site. This is usually illustrated in

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the form of a volcano plot [12, 13]. An alloy will have an adsorption energy somewhere in between its components. Using this principle, alloys may achieve properties similar or sometimes superior to those of pure precious metals [8, 14–16]. However, it can be challenging to synthesize the desired alloyed nanoparticles in the right ratio and uniform distributed in the catalyst.

Metal-organic frameworks (MOFs) have attracted a lot of attention recently, due to the ease of synthesis, high porosity and surface area [17, 18]. MOFs are easily made by mixing a metal salt with an organic linker in an appropriate solvent. Recently, there has been interest in the use of MOF derivatives as the structural template for making a new class of heterogeneous catalysts [19-21]. MOF derived carbon materials have been known at least since 2007, where MOF-5 was pyrolysed with polymerized furfuryl alcohol to make a nanoporous carbon with good hydrogen uptake and electrochemical properties [22]. Since then, different types of MOF-derived nanomaterials have been tested for use in sensing, gas-/energystorage and catalysis with good performance [23, 24]. One method is to carbonize the MOF, creating a carbonaceous support material. Due to the high structural stability of the original MOF, much of the structure, pore volume and specific surface area is preserved after carbonization [25–27]. The material gains increased thermal and chemical stability, but loses the functionalities of the ligands [28-30]. The carbonization process also help with the reduction of the metal ions present in the ZIF structure to form metal nanoparticles. MOF-derived carbons have been tested for several purposes such as oxygen reduction reaction, Li-ion batteries, gas storage and as a support material for heterogeneous catalysts [31–33].

Zeolitic imidazolate framework (ZIF) materials are a group of MOFs with attractive properties, due to their structural similarities to zeolites [34, 35]. A great number of ZIF structures have been reported over the last decade, mimicking both known zeolite structures and added new topologies [21, 35, 36]. Synthesis of ZIF with more than one metal and with different metal ratios can be difficult and time-consuming. By using incipient-wetness impregnating on the porous ZIF with a secondary metal precursor before carbonization, bimetallic alloy nanoparticles are expected to be formed inside the new carbon support. Previously a 50/50 CoNi alloy has been synthesized using a similar procedure [37]. Data from XRD indicated the formation of uniform alloy nanoparticles between Co and Ni in the carbonized ZIF-67.

Herein we present a simple way to synthesize cobalt-copper nanoalloys on nitrogen-doped carbon in

a variety of loadings using ZIF-67 as a carbon-, cobalt-, nitrogen-containing platform. Cobalt containing ZIF-67 was impregnated with a different Cu solution before carbonization. In total were seven different catalysts synthesized with different amounts of cobalt and copper. The synthesized materials were characterized using XRD, TEM, SEM, XRF and nitrogen physisorption. The catalytic activities of the produced materials were compared using a model reaction, conversion of cyclohexanone to the corresponding silyl ether. The reaction is typically run using a homogenous precious metal catalyst [38–40].

The synthesis method benefits from the presence of nitrogen in the 2-methylimidazole in the ZIF, creating a natural nitrogen-doping of the resulting carbon. Nitrogen-doping of carbon is a common way of tuning the electronic properties of carbon materials, often utilized in the development of electro-catalysts for fuel cells and other electronic devices [41]. However, the positive effect of nitrogen-doping is not limited to electrochemical reactions as number of other reactions have seen increased yield due to the presence of nitrogen [42–46].

2 Experimental Section

A total of seven types of catalysts were synthesized with expected Co/Cu ratios of 99:1, 19:1, 9:1, 3:1, 1:1 as well as a pure Co and pure Cu variant. The samples are labelled as $Co_xCu_y@NC$, were x and y indicate the expected amount of Co compared to Cu and NC = nitrogen-doped carbon. According to the empirical formula, $C_8H_{10}N_4Co$, the ZIF-67 is expected to contain 26.7 wt% Co before carbonization, which serves as the basis for the calculating the amount of Cu needed. The basic procedure for ZIF-67 has been used in previous work [37].

2.1 Materials

All chemicals were obtained from Sigma-Aldrich with no further purification. 2-methylimidazole, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O > 98%), methanol (MeOH ≥ 99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O ≥ 99%), copper(II) nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O), cyclohexanone, dimethylphenylsilane (HSiMe₂Ph ≥ 98%), toluene, dibenzylether, ethylacetate, D-chloroform (CDCl₃ 99.8 atom % D), triethylsilane (HSi(C₂H₅)₃ 99%).

2.2 Synthesis of ZIF-67 and ZIF-8

ZIF-67 was synthesized according to previous work by Lou et al. [47]. In a 1L Erlenmeyer flask a solution of 2-methylimidazole in MeOH (3.2840 g in 250 mL) and a solution of $Co(NO_{3})_2 \cdot 6 H_2O$ in MeOH (2.9104 g in 250 mL) were mixed at room temperature. The mixture was stirred for 5 min, aged for 24 h. The cobalt containing ZIF-67 was collected by centrifugation and dried in an oven at 80 °C. The typical yield was 0.5 g.

ZIF-8 was synthesized using the same metal to ligand ratio. A solution of 2-methylimidazole in MeOH (3.2840 g in 250 mL) and a solution of $Zn(NO_3)_2 \cdot 6H_2O$ in MeOH (2.9748 g in 250 mL) were mixed at room temperature. The mixture was stirred for 5 min, aged for 24 h. The zinc containing ZIF-8 was collected by centrifugation and dried in an oven at 80 °C. The typical yield was 0.8 g.

2.3 Synthesis of Co_xCu_y@NC

Different amounts of Cu(NO₃)₂·2.5H₂O were dissolved in 85 μ L MeOH. Dried ZIF-67 was impregnated to incipientwetness to make each of the desired Co/Cu ratios. The resulting powders were flushed at room temperature using Ar for 30 min. followed by carbonization at 675 °C heated at a rate of 5 °C/min. in Ar for 3 h.

2.4 Synthesis of Cu@NC

As a reference material Cu@NC was synthesized. A solution of Cu(NO₃)₂·2.5H₂O in MeOH (45.4 mg in 340 μ L) was prepared. 170 μ L of the solution was used for incipient wetness impregnation of the dried ZIF-8. The resulting powder was followed by flushing in Ar for 30 min. at room temperature. The impregnated powder was then carbonized at 900 °C heated at rate 5 °C/min. for 3 h. The

increased temperature is required in order to remove the Zn in the ZIF-8 and incorporate Cu in the structure.

2.5 Material Characterization

XRF data was acquired using a PanAnalytical epsilon 3-XL directly on the powdered catalyts without any prior treatment. TEM images was acquired on a FEI Tecnai T20 G2 instrument from Thermo Fisher Scientific. Powdered samples were placed on holey carbon grids with no prior treatment. SEM was carried out on a FEI Quanta 200 ESEM FEG on powdered samples placed on carbon grids. XRD was acquired using Cu-K α from a focusing quartz monochromator and a Huber G670 Guinier camera. The samples were loose powders and run for one hour.

2.6 Catalytic Measurements

The catalytic performances of the catalysts were compared using the hydrosilylation reaction of cyclohexanone. The experiments used solutions of 1 mmol cyclohexanone/mL and 1.2 HSiMe₂Ph/mL in toluene prepared in glovebox together with 10 mg Co_xCu_y@NC catalyst. The vials were sealed with teflon caps and allowed to react outside the glovebox at 90 °C, stirred at a rate of 600 RPM. The products were quantified by NMR. ¹H-NMR data was acquired on a Bruker Ascend 400 (400 Hz).

3 Results and Discussion

Each of the seven $Co_x Cu_y @NC$ catalysts synthesized were characterized using a number of different techniques along with the original ZIF-67 material for comparison.

In order to form the cobalt–copper alloyed particles on nitrogen-doped carbon, the ZIF-67 impregnated with Cu precursor was carbonized in Ar at high temperature.



Fig. 1 Schematic representation of a typical synthesis of Cu-doped carbonized ZIF-67



Fig. 2 N₂-physisorption isotherm of synthesized ZIF-67 (a) and Co₉Cu₁@NC-675 (b)

The decomposition during carbonization was investigated using TGA (see Supporting Information, S1). ZIF-67 starts to decompose at around 480 °C and has lost about 40% of its total mass at 600 °C. Based on ICP-OES the content of pure ZIF-67 is about 26 wt% as is expected from it empirical formular ($C_8H_{10}N_4Co$). After carbonization at 600 °C, the Co content increases to about 30 wt% (see Supporting Info, S2) (Fig. 1).

Nitrogen physisorption of the synthesized ZIF-67 and the derived carbon material is shown in Fig. 2. ZIF-67 originally had a typical type I isotherm indicating a microporous material. After impregnation with 10% copper and subsequent carbonization, the isotherm becomes a type II with a clear hysteresis loop indicative of mesopores in the structure.

ZIF-67 shows a high surface area of 1364 m²/g (BET), and a pore volume of 0.762 cm³/g (Single Point Adsorption) similar to what has been reported in other work [19, 48]. After impregnation and carbonization, the surface area and total pore volume drops significantly. $Co_9Cu_1@NC-675$ had a BET surface area of 244 m²/g and a total pore volume of 0.079 cm³/g. BJH adsorption and comparison of isotherms at different copper loadings can be found in Supporting Information S3–S5.

The change in structure from ZIF-67 to porous carbon support is apparent in SEM. In Fig. 3 it is clear that the polyhedral shape of the original ZIF-67 is distorted after



Fig. 3 SEM images showing the polyhedral shape of the catalysts, which clearly seen for ZIF-67 (a), however it has been somewhat distorted after carbonization at 675 °C as seen for $Co_9Cu_1@NC$ (b)



Fig.4 XRD pattern of synthesized nitrogen-doped carbon catalyst. **a** Shows the full range of angles measured, showing none of the many characteristic peaks of ZIF-67 between 5 and 40° . **b** Features a zoom-

Table 1 CoCu ratios determined using XRF

Entry	Catalyst	Cu(NO ₃) ₂ ·2.5H ₂ O added/100 mg ZIF-67	Cu/Co ratio
1	Co@NC	_	_
2	Co99Cu1@NC	1.05 mg	1/65.67
3	Co ₁₉ Cu ₁ @NC	5.55 mg	1/15.67
4	Co ₉ Cu ₁ @NC	11.7 mg	1/7.93
5	Co ₃ Cu ₁ @NC	35.1 mg	1/2.62
6	Co ₁ Cu ₁ @NC	105.2 mg	1/0.90
7	Cu@NC	_	_

impregnation with Cu and subsequent carbonization. The overall particle size seems reduced from the original 1 μ m to about 700 nm.

XRD was performed to confirm the formation of CoCu alloyed particles. Each of the catalysts (Fig. 4) show characteristic peaks of Co at 44.32, 51.70, 75.8 and 92.1°. At higher loadings of Cu, its (111) peak becomes visible at 43.31°, along with additional peaks at 50.4, 74.1, 89.9 and 95.2°. The Co (111) peak at 44.32° shifts towards a lower diffraction angle of 44.20°, when the metal content is above 25% Cu. None of the typical peaks associated with ZIF-67 between 5 and 40° can be seen here [42, 49]. The peaks were identified using data from the ICDD. According to Vegard's Law, the location of the alloy peak can be linearly related to its composition. Based on the Co



in on the Co(111) and Cu(111) peaks. The Co(111) is clearly seen shifting downward at higher Cu loadings

(111) peak, the particles were estimated to contain roughly 10% Cu. The Cu (111) peak is not notably shifted from the location of pure copper, indicating the presence of pure copper particles. Even with an equal amount of Co and Cu, the nanoparticles seemingly consist of CoCu particles containing 10% Cu and a larger amount of separate almost pure Cu nanoparticles.

Characterization using XRF was used to confirm the CoCu ratio of the synthesized catalyst (see Table 1). The results show good control over CoCu ratio using simple incipient wetness impregnation. In general the amount of Co is lower than expected. This may be due to a slightly lower content of Co in the parent ZIF-67 material. The nitrogen species present in the structure were examined using XPS (see Supporting Info, S4 and S5). The nitrogen content in the surface was found to be about 4% for the carbonized ZIF (Entry 1), while the materials containing added copper (Entry 2–6) had an increased content ranging from 7.8 to 11%. The nitrogen peaks indicated equal amounts of graphitic and pyradinic nitrogen with the exception of Entry 1, which also showed a fair amount of pyrrolic nitrogen (31.9%) and less graphitic nitrogen (12.5%).

TEM images of the carbonized ZIFs show that the dodecahedral shape of ZIF-67 is retained after carbonization (Fig. 5). This matches what has previously been reported by Zou et al. [50] The size of the dodecahedra's range from 0.6 to 1.4 μ m, seemingly increasing in size with higher loadings of Cu. The metal nanoparticles are clearly seen distributed



Fig.5 TEM images of all ZIF-67 derived catalysts. As more Cu is added, the polyhedral structure starts to break down. **a** Co@NC, **b** Co₉₉Cu₁@NC **c** Co₁₉Cu₁@NC **d** Co₉Cu₁@NC **e** Co₃Cu₁@NC **f** Co₁Cu₁@NC. (Cu@NC can be found in Supporting Info S10–S12 along with histograms and additional images of all catalysts)

 Table 2
 Experimental results from hydrosilylation of cyclohexanone

across the carbon support. The size of the metal nanoparticles mainly range from 8 to 20 nm.

TEM also shows the influence of the higher Cu loading on the overall structure of the carbon matrix. The dodecahedral structure seemingly increases in size with higher loadings of Cu. As the amount of added Cu increases, the carbon structure loses much of its dodecahedral structure as can be seen from $Co_3Cu_1@NC$ and $Co_1Cu_1@NC$. STEM–EDS shows how the large particles generated when doping with more Cu are mostly pure Cu particles, while at lower loadings a good dispersion of both Cu and Co is seen (see Supporting Info, S13-14).

3.1 Hydrosilylation of Cyclohexanone

In order to compare the activities of the synthesized Co_xCu_y@NC catalysts, the hydrosilylation of Cyclohexanone (1a) was chosen as a model reaction. The same amount of catalyst was used for each of the reactions. The results from the hydrosilylation of cyclohexanone (1a) can be seen in Table 2. Using the carbon catalyst derived directly from ZIF-67 (Entry 1) yields 21% of the silyl ether product under the given conditions. The purely copper containing Cu@NC derived from ZIF-8 (Entry 7) affords a much lower yield of only 9%. Similar, low yields where observed for commercial Cu and Pt on carbon (Supporting Info S17). A clear improvement in reactivity is seen when the two are combined to form CoCu alloy nanoparticles. Even Co₉₉Cu₁@NC shows an increase in yield from 21 to 35% compared to Co@NC. When using much higher Cu loadings like those found



Entry	Catalyst	Yield (%)	Conversion (%)
1	Co@NC	21	38
2	Co ₉₉ Cu ₁ @NC	35	41
3	Co ₁₉ Cu ₁ @NC	38	45
4	Co ₉ Cu ₁ @NC	72	72
5	Co ₃ Cu ₁ @NC	100	100
6	Co ₁ Cu ₁ @NC	100	100
7	Cu@NC	9	29

Yield based on NMR



Fig.6 Time study of $\mathrm{Co}_9\mathrm{Cu}_1@\mathrm{NC}$ for the hydrosilylation of cyclohexanone

in $Co_3Cu_1@NC$ and $Co_1Cu_1@NC$ complete conversion is achieved.

Co₉Cu₁@NC was selected for a time study (Fig. 6) and scope for a range of hydrosilylation reactions (Table 3). The time study shows the reaction occurs with no induction period and fits with an overall 1st order reaction (Fig. 7). Cyclohexanone (1a) gave good yields under these conditions. However, the addition of a t-butyl group brought the yield down to a few percent (1b). Acetophenone readily reactants to form the silvl ether. Induction effects affects the yield as demonstrated by the addition of different groups in the para position. A methyl group brings the silvl ether yield down to 75% (1d). The combination of a longer alkyl chain on the ketone and an ether group in the para position lowers the yield down to 57% (1e). The introduction of electron withdrawing group, fluorine, brings the yield down to 46% (1f). Additionally, when a large bulky group was added at the end of the alkyl, the yield was lower than for any of the other acetophenones (1g). TEM of the Co_oCu₁@NC after reaction show no notable differences to the fresh catalyst (Supporting Info, S15-16). The catalyst show partly deactivation when reused first time. However, the deactivation seemed to stabilise when reused further times (Supporting S18).

4 Conclusion

MOF derived carbon materials combine the advantages of a stable porous materials with a high metal loading. The present work shows that using simple preparation methods, bimetallic CoCu alloy nanoparticles incorporated in mesoporous carbon can be synthesized with good control of the metallic ratio. The nanoparticles are well-distributed with an average size of about 10 nm. The $Co_xCu_y@NC675$ catalysts show high yield for a simple hydrosilylation reaction compared to catalysts containing only Co or Cu. Under relatively mild conditions, complete conversion of cyclohexanone to the silane when the CuCo ratio is 1/2.62 or above.



Yield based on NMR





Fig. 7 Linear fit of time study indicating an overall 1st order reaction hydrosilylation of cyclohexanone

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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