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Cobalt-nickel alloy catalysts for hydrosilylation of ketones synthesized by utilizing metal-organic framework as template

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In this article, we report an approach to synthesize alloy Co-Ni nanoparticles encapsulated in carbon by utilization of the MOF, ZIF-67, as a sacrificial template. The alloy CoNi materials are synthesized by incipient wetness impregnation of cobalt-containing ZIF-67 with nickel(II) nitrate followed by carbonization. The formation of alloy nanoparticles was verified by XRD and TEM analysis showed that they are distributed evenly throughout the entire material. The carbon encapsulating the alloy nanoparticles is N-doped and graphitic according to XPS analysis. Further characterization by ICP, N_2-physisorption, and SEM imaging was also performed. The CoNi materials exhibited promising activity in the catalytic hydrosilylation of ketones. A carbonization temperature of 800 °C provided the best catalyst for this transformation. The reaction conditions were optimized, different silanes tested, a time study conducted, and the heterogeneity of the catalysis assessed with different tests. Finally, a substrate scope of various ketones was examined.

Introduction

Metal-organic frameworks (MOFs) have attracted much attention due to their high porosity, surface area, and easily tunable chemical structure.[1,2,3,4] As a consequence of these features, MOFs have found applications in various fields such as chemical sensoring[5], gas storage[6,7], photocatalysis[8,9] and catalysis[3,10]. One of the remaining challenges associated with the use of MOFs as catalysts is their often moderate thermal stability. Accordingly, as an alternative approach to catalyst synthesis, MOFs have been used as structural templates and source of carbon for the formation of metal nanoparticles encapsulated in a porous matrix.[11] This process is facilitated by carbonization of the MOF. In contrast to the parent MOFs (non-carbonized), these encapsulated metal nanoparticles typically possess improved chemical and thermal stability required for catalytic reactions and efficient catalyst recycling. Most of the reported studies focus on carbonization of monometallic MOFs such as the isostructural Zn^{2+}-containing ZIF-8 and Co^{2+}-containing ZIF-67, where the metal ions are linked by 2-methylimidazole.[12,13,14]

Recently, the use of catalysts consisting of metal nanoparticles which are alloys of abundant, non-noble metals has received considerable due to the intriguing properties of these materials.[15,16,17] Alloying non-noble metals together may achieve the desired activity and selectivity often observed by using precious metals as seen in the synthesis of ammonia with a cobalt/molybdenum alloy.[18] In the case of alloy nanoparticles between cobalt and nickel, they have shown enhanced catalytic activity in CO_2 dry-reforming[19,20], water splitting[21], oxygen evolution reaction[22], and H_2 release[23]. However, in terms of their use in reactions for synthetic organic chemistry, very few examples exist. Recently, our group have published that alloy CoNi nanoparticle are active catalysts for a series of organic reactions, including silylative pinacol coupling reactions and double bond migrations.[24,25]

In the synthesis of alloy CoNi nanoparticles, ZIF-67 is of interest due to its inherent cobalt content, which during carbonization facilitate the formation of cobalt nanoparticles encapsulated in porous N-doped carbon. These nanoparticles are ideal for heterogeneous catalysis.[11,26] However, only few attempts to synthesize alloy metal nanoparticles by introducing additional metals into the ZIF prior to the carbonization process are reported and no CoNi alloys accessed from ZIF-67 are reported.[27]

Reduction of ketones by hydrogenation or hydrosilylation is an important and widely used transformation in the production of fine chemicals, such as pharmaceuticals.[28] The hydrosilylation approach avoids the use of high pressures, which can be a requirement for hydrogenations. For ketone hydrosilylation, homogeneous precious metal catalysts have typically been used.[29] However, significant recent advances in homogeneous base metal catalysis has led to the development of highly efficient catalytic systems based on these inexpensive metals.[30] While selectivity and activity is often higher in homogeneous catalysis, heterogeneous catalysis offers significant advantages in terms of recyclability, ease of catalyst separation, and robustness. Thus, the development of heterogeneous base metal catalysts for hydrosilylation of ketones is of high importance. Only a few reports exist on heterogeneous base metal catalysed ketone hydrosilylation.[31]

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Herein, we report a new way to synthesize alloy cobalt-nickel alloys by the utilization of ZIF-67 as sacrificial template, and source of carbon, nitrogen, and cobalt. The porous structure of ZIF-67 facilitates the introduction of nickel into the pores by incipient wetness impregnation before carbonization. Carbonization of the impregnated ZIF-67 promotes the formation of alloy cobalt-nickel nanoparticles encapsulated in a porous carbon matrix. The synthesized alloy materials are abbreviated CoNi@NC$_x$, where NC is porous N-doped carbon and X represents the carbonization temperature, which was either 550, 675 or 800 °C (Figure 1). The resulting material was assessed in the hydrosilylation of ketones. The assessment involves optimization of the reaction conditions, time study, recycling experiment, ketone scope, and silane scope.

Experimental

Synthesis of ZIF-67:[1]

The synthesis of ZIF-67 was adapted from David Lou *et al*.[32]: In short, 2.91 g (10 mmol) cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and 3.28 g (40 mmol) 2-methylimidazole was dissolved separately in 250 mL MeOH. The two solutions were mixed by adding the 2-methylimidazole solution to the cobalt(II) nitrate solution. The mixture was stirred for 5 min, aged for 72 hours, collected by centrifugation, and dried in an oven overnight at 80 °C. 500 mg ZIF-67 was obtained; 23% yield based on cobalt.

Synthesis of Co@NC:

200 mg ZIF-67 was carbonized in a tube furnace at 800 °C for 3 hours with a heating ramp of 5 °C/min. This yielded 120 mg of cobalt nanoparticles encapsulated in N-doped carbon (Co@NC) as a black powder.

Synthesis of CoNi@NC$_x$:

200 mg ZIF-67 (0.9 mmol cobalt) was impregnated with nickel by dissolving 262 mg (0.9 mmol) $Ni(NO_3)_2{\cdot}6H_2O$ in 140 µL MeOH. The resulting powder was carbonized in a tube furnace at 550, 675, or 800 °C for 3 hours with a heating ramp of 5 °C/min. This yielded 130 mg of alloyed cobalt-nickel nanoparticles encapsulated in N-doped carbon (CoNi@NC) as a black powder.

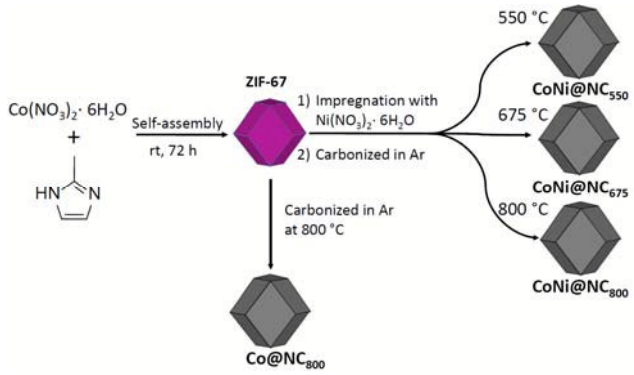

Fig. 2 Schematic overview of the different materials synthesized in this study.

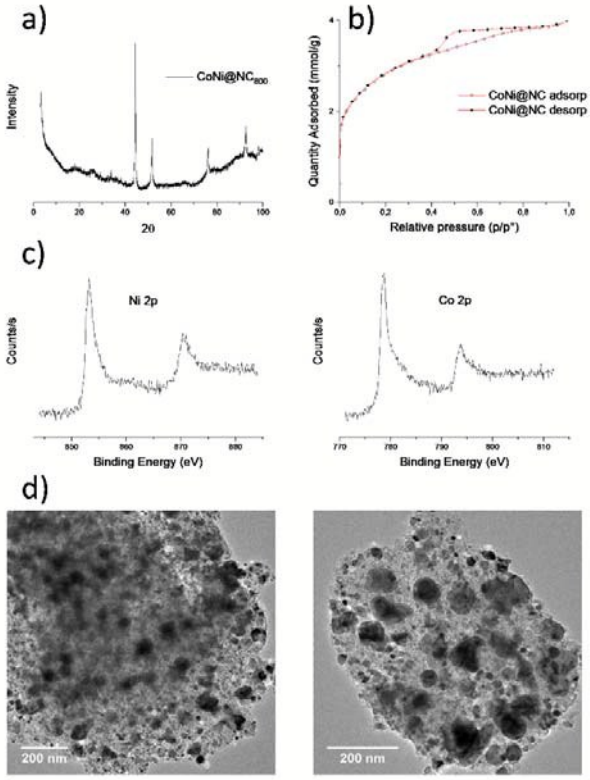

Fig. 1 Characterization of CoNi@NC800. The figure includes a) XRD diffractogram, b) N2-physisorption isotherm, c) XPS analysis of Co and Ni, and d) TEM images of the catalyst.

Results and characterization

For CoNi@NC$_{800}$, the XPS analysis, N_2-physisorption isotherm, the X-ray diffraction (XRD) diffractogram, and TEM images of are presented in Figure 2. The characterization data for the other materials are found in supporting information. The XRD diffractogram (Figure 2a) shows that the original crystalline phase of the ZIF-67 crystals have completely converted into a carbon material. Furthermore, only one peak at 2Θ ≈ 44 correlating to a 111-difraction is found in the diffractogram suggesting the formation of uniform alloy nanoparticles between cobalt and nickel, and not individually monometallic nanoparticles. Additionally, the 111-diffraction peak from the alloy material is slightly shifted compared to the monometallic cobalt material, which also suggests the formation of alloy nanoparticles according to Vegard's law.[33] These observations are consistent with a previously reported CoNi alloy material synthesized by carbonization of a mixed metal-EDTA salt.[25,34] Diffractograms of the other materials are found in Figure S5.

The N_2-physisorption adsorption/desorption isotherm for CoNi@NC$_{800}$ shown in Figure 2b is best described as a mixture of type I and IV by the IUPAC nomenclature with the presence of a hysteresis indicating the mesoporous nature of the carbon material.[35] The estimated pore volume, microporous volume and BET surface for all the synthesized materials are summarized in Table 1. It is clear that the original pore volume,

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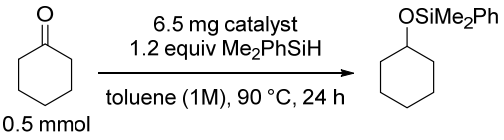
Table 1 Values obtained from N_2-physisorption from the four different catalytic materials and the template ZIF-67.

Catalyst	Pore volume[1] (cm^3/g)	Microporous volume[2] (cm^3/g)	Surface area[3] (m^2/g)
ZIF-67	0.762	0.664	1364
CoNi@NC550	0.132	0.096	232
CoNi@NC675	0.152	0.072	246
CoNi@NC800	0.135	0.024	213
Co@NC800	0.184	0.043	283

[1] Single point read at p/p_0. [2] t-plot method. [3] BET method.

Table 2 Catalytic activity tests for the synthesized materials.



Entry	Catalyst	Conversion (%)	Yield (%)
1	ZIF-67	3	1
2	CoNi@NC_{550}	80	68
3	CoNi@NC_{675}	71	62
4	CoNi@NC_{800}	86	73
5	Co@NC_{800}	30	3

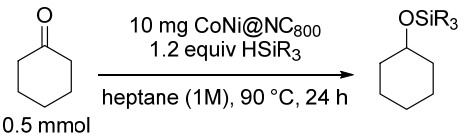
Yield based on ^{1}H NMR using 0.5 equivalents of dibenzyl ether as standard.

microporosity and BET surface area of ZIF-67 is lost during the impregnation and carbonization process.

The different elemental species present in the carbonized materials were assessed by XPS analysis for cobalt, nickel, carbon, and nitrogen. The spectra are in the supporting information (Figure S8-11) but the 2p scan for cobalt and nickel are in Figure 2 for the CoNi@NC_{800} catalyst. The spectra show the presence metallic Co and Ni at 779.7 eV and 852.6 eV, respectively. For the samples carbonized at 550 and 675 °C, a larger proportion of metal oxide is observed which may be caused by the presence of smaller metal nanoparticles providing more surface that can be oxidized.[36] Examination of the carbon present in the catalyst by XPS suggests that the majority is sp^2-hybridized carbon, i.e. graphitic. This is exemplified by the 1s peak for carbon which is present at 284.8 eV where graphitic carbon is reported at 284 eV.[37] XPS spectra of nitrogen indicates that multiple species are present in the catalysts carbonized at 800 °C. The 1s peaks from nitrogen are present at both 399 eV and 401 eV which correlates to pyridinic nitrogen, and either pyrrolic or graphitic nitrogen or a combination of both.[38] As for the materials carbonized at 550 or 675 °C, the pyridinic nitrogen species are more profound. Additional investigation of the atom configuration of the CoNi@NC_{800} catalyst is shown in Figure S8.

ICP-OES analysis of CoNi@NC_{800} reveals that 67% of the catalyst is metal with a Co:Ni ratio of 60:40. This suggests that some of the added nickel during the incipient wetness impregnation is not incorporated into the final material.

Table 3 Screening of different silanes conducted under optimized conditions.



Entry	$HSiR_3$	Conversion (%)	Yield (%)
1	Me_2PhSiH	100	100
2	Et_3SiH	85	50
3	$EtMe_2SiH$	100	78
4	$MePh_2SiH$	51	36
5	Ph_3SiH	11	0

Yield based on ^{1}H NMR using 0.5 equivalents of dibenzyl ether as standard.

The TEM image for the CoNi@NC_{800} catalyst in Figure 2 shows the distribution of CoNi alloy nanoparticles throughout all of the material. However, due to the high metal content, partial particle agglomeration is occurring, which leads to a broad size distribution of metal nanoparticles ranging from 10-75 nm.

SEM images of the carbonized CoNi@NC_{800} show that the characteristic rhombic dodecahedron shape of ZIF-67 is not preserved after the carbonization process. To analyse the origin of the structural change, carbonized ZIF-67 without the nickel impregnation step was also analysed and showed no structural change. This implies that a structural change is occurring because of the impregnation with nickel prior to the carbonization process. The SEM images are in Figure S13-14.

Initially, the different materials were compared, and the CoNi@NC_{800} catalyst showed the most promising results (Table 2). The subsequent optimization of the reaction conditions revealed that better selectivity and complete conversion of cyclohexanone in 24 hours could be obtained in heptane with 10 mg of catalyst and only a small excess of Me_2PhSiH (Table 3, entry 1). Additional information about the optimization process is presented in Table S2-3 in the supporting information.

The influence of the silane was investigated by screening five different silanes as shown in Table 3. Me_2PhSiH gives the highest yield and selectivity towards the hydrosilylation product (entry 1). Other silanes show good to high activity, except the bulky Ph_3SiH (entry 5). It appears that the introduction of more bulky groups to the silane decreases the activity of the hydrosilylated product by comparing entry 1, 4, and 5 (Me_2PhSiH > $MePh_2SiH$ > Ph_3SiH).

The time study presented in Figure 3 shows an induction period of approximately 4 hours where no catalytic activity is observed. It is also evident from the time study that 24 hours is required for a complete reaction with cyclohexanone under the optimized conditions.

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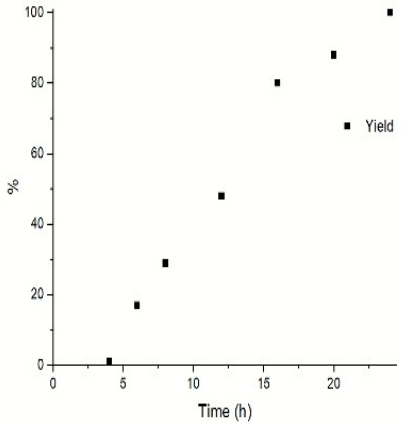


Fig. 3 Time study presented with yield as a function of reaction time. The study was conducted under optimized conditions with cyclohexanone (Table 3, entry 1).

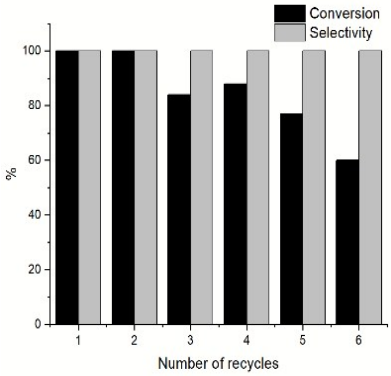
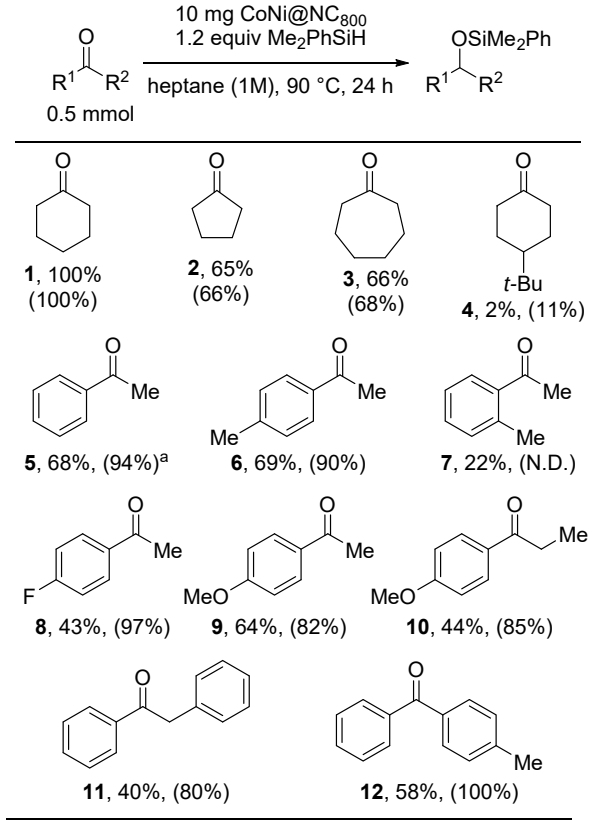


Fig. 4 The catalyst was recycled six times. The recycling of the catalyst was facilitated by separating the catalyst from the reaction mixture by a magnet, which exploited the magnetic properties of the catalyst

In order to examine the recyclability of the catalyst, seven consecutive reactions (six recycles) with the same catalyst were performed (Figure 4). The magnetic properties of the catalyst allow for easy recycling by a simple magnetic filtration. Over the course of seven reactions, the catalyst maintains 100% selectivity, but a decrease in conversion from 100% to 60% was observed. By analysing the catalyst after the seventh reaction by TEM (Figure S15), it is evident that the alloy metal nanoparticles have agglomerated which is a likely explanation for the deactivation. We also investigated the possibility of metal leaching during the reaction by ICP-OES analysis of two reaction mixtures, which were filtered after 24 hours. In both cases, the cobalt and nickel content in the filtrate was below detection limit (equal to a blank sample). Finally, a hot filtration test was performed to support the suggested heterogeneous nature of catalysis. After 12 hours of reaction, the reaction mixture was filtered while hot and filtrate kept at 90 °C for additional 8 hours. No additional conversion was observed in the filtrate, hence indicating that the catalysis is heterogeneous.

Table 4 Scope of different ketones for the hydrosilylation reaction



Yields are based on ^{1}H NMR using 0.5 equivalents dibenzyl ether as standard. Conversion of the ketone is shown in parenthesis. a) 2.0 equivalents Me_2PhSiH.

For a single reaction, the TON and TOF is 11 and 0.46 h^{-1}, respectively.[39] However, taking into account the facile recycling, a summative TON of 67 is obtained after seven consecutive reactions. Albeit higher TONs can be obtained with other base metals, the obtained TON is more than three times greater than a recent report using a homogeneous nickel catalyst (at 100 °C).[40]

In order to examine the generality of the developed methodology, a range of ketones was subjected to the reaction conditions (Table 4). Cyclopentanone (**2**) and cycloheptanone (**3**) displayed excellent selectivity with good yields in both cases, thus demonstrating only a small influence from the ring-size. A sterically hindered *tert*-butyl-substituted cyclohexanone (**4**) led to apparent inhibition of the activity. The yield of the hydrosilylated product from acetophenone (**5**) was moderate under standard conditions but was improved by using 2.0 equivalents of Me_2PhSiH instead of 1.2 equivalents. A methyl group in the *para* position of acetophenone increased activity and yield, whereas a methyl in the *ortho* position decreased activity and yield (**6**-**7**). *p*-Fluoroacetophenone (**8**) is very active with 97 % conversion and moderate yield of the hydrosilylated product. In contrast, the selectivity is markedly improved for *p*-methoxyacetophenone (**9**) which gives a good yield of the hydrosilylated product. However, the introduction of sterical hindrance decreases the yield and activity (**10**). A comparable

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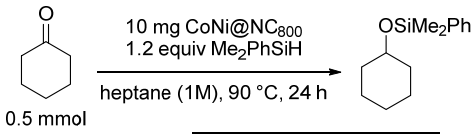
result was obtained with 2-phenylacetophenone (**11**). Finally, the diaryl ketone (**12**) provided 58% yield of the hydrosilylated product.

In a previous extensive mechanistic study, we obtained evidence for the formation of silyl radicals from $HSiEt_3$ mediated by a related NiCo@NC catalyst.[24] In order to test for a radical pathway with the catalyst reported here, we performed the standard reaction in the presence of the radical inhibitors BHT and TEMPO (Scheme 1). The addition of 1.2 equivalents BHT or 20 mol% TEMPO did not affect the reaction outcome. In addition, no TEMPO adducts from radical trapping was observed at the end of the reaction.[41] In combination with the heterogeneity tests and sensitivity to sterical hindrance, we propose that the reaction follows the Ojima mechanism[42], likely with the ketone substrate coordinating to the surface of the catalyst, which can explain the sensitivity to sterical hindrance.

Scheme 1. The effect of radical inhibitor and scavenger on the reaction outcome.



Additive	Yield (%)
no additive	100
1.2 equiv BHT	100
20 mol% TEMPO	>95

Conclusions

Alloy CoNi nanoparticles encapsulated in porous carbon were successfully synthesized by utilizing ZIF-67 as a sacrificial template. The synthesis was facilitated by incipient wetness impregnation of nickel(II) nitrate into the pores of ZIF-67 followed by carbonization under an argon atmosphere.

XRD confirms the presence of alloy nanoparticles, and their unique catalytic activity was highlighted by comparing the monometallic $Co@NC_{800}$ catalyst with the $CoNi@NC_x$ materials. The porous carbon in the catalyst is N-doped and graphitic. A structural change from the characteristic rhombic dodecahedron shape occurred as a consequence of the incorporation of nickel during the carbonization process. The alloy materials displayed good catalytic activity in the hydrosilylation of cyclohexanone. Albeit higher activities can be accessed with some homogeneous base metal catalysts, easy recycling of the developed CoNi@NC catalyst can provide TONs which surpass a comparable homogeneous nickel catalyst. For a range of ketones good-to-high yields of the hydrosilylation products were obtained. A hot filtration experiment and ICP-OES supported the heterogeneous nature of catalysis and absence of leaching. However, slow deactivation by agglomeration was observed by TEM. Finally, the reaction outcome was unaffected by the presence of radical inhibitors and we propose a surface reaction proceeding through the Ojima mechanism, i.e. without radical intermediates.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes

[1]Characterization of the synthesized ZIF-67 crystals is in the supporting information.

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