Supporting information

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

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1. Experimental

I. Chemicals

All chemicals used in the catalyst synthesis and in the catalytic reactions were reagent grade and utilized without further purification. $Co(NO_3)_2 \circ 6H_2O$, $Ni(NO_3)_2 \circ 6H_2O$, 2-methylimidazole, Et_3SiH , Me_2EtSiH , Ph_3SiH , Ph_2SiH , cyclopentanone, cyclo-hexanone, cycloheptanone, *tert*-butyl cyclohexanone, cyclohexyl methyl ketone, 4-heptanone, 2,4-dimethyl-3-pentanone, acetophenone, 4'-methylacetophenone, 4'-methylacetophenone, 4'-methylacetophenone, 4'-methylacetophenone, 4'-methyl-benzophenone and cyclopropyl 4-methoxyphenyl ketone were all purchased from Sigma Aldrich, whereas $MePh_2SiH$ was bought from Alfa Aesar and Me_2PhSiH from Fluorochem.

X-ray Powder diffraction (XRPD) were measured with a Cu-K α radiation source on a HUBER G760 Guinier camera. N₂-physisorption was conducted on a Micrometrics 3Flex instrument at 77 K. Samples for N₂-physisorption were degassed 24 hours before the analysis on a Micrometrics VacPrep 061 Sample Degas System at room temperature for ZIF-67 and 200 °C for the carbonized materials. TGA was performed on a Mettler Toledo TGa/DSC 1 STARe System. XPS was done with a spot size of 400 µm with an Al alpha X-ray source with 10 scans per element. Surface edging in XPS was conducted with an energy source of 3000 eV with an exposure time of 30 seconds. SEM images were taken on a Quanta 200 ESEM FEG microscope from FEI. TEM images were obtained from a Technai T20 G2 microscope from TEI. ICP-OES was conducted on an iCAP 7000 Plus Series from Thermo Scientific with a Teledyne CETAC ASX-560 autosampler. ¹H-NMR samples were measured on a Bruker Ascend 400 (400 Hz). All synthesized catalyst materials were stored under a protective argon atmosphere except ZIF-67, which was stored in atmospheric air.

II. Synthesis of ZIF-67

The synthesis is adapted from the report by David Lou et al.¹: 2.91 g (10mmol) Cobalt(II) nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O)$ was dissolved in 250 mL methanol. Similarly, 3.28 g (40 mmol) 2-methylimidazole was dissolved in 250 mL MeOH. The two solutions were mixed by adding the 2-methylimidazole solution to the cobalt(II) nitrate solution. The resulting purple mixture was shaken for 5 min and purple precipitate was observed. The mixture was left to age for 72h. The precipitate was isolated by centrifugation at 10000 rpm for 10 min and washed 3 times with MeOH. The washed powder was dried and stored in an oven at 80 °C overnight before use. 500 mg ZIF-67 was obtained; yield = 22.5% based on Co.

III. Catalytic tests

Inside a glovebox, the catalyst was added to a 4 mL vial containing a stirbar. In another vial, a stock solution was made of 1 Mketone and 1.2 M silane with a total volume of 1 mL in either heptane or toluene. 0.5 mL of the stock solution was added to the vial with the catalyst and the mixture was sealed with a PTFE-lined screw cap. Outside the glovebox, the reaction mixture was placed in an aluminum-heating block at 90 °C with magnetic stirring (600 rpm) for 24 h.

After 24h, the mixture was cooled down to room temperature and 1 mL of a 0.25 M dibenzyl ether in ethyl acetate was added as a NMR standard. Afterwards, 0.5 mL of the reaction was filtered and concentrated under vacuum to remove some of the ethyl acetate. The resulting solution was analyzed by ¹H-NMR using chloroform-d as the solvent.

IV. Recycling

In a recycling experiment, the same procedure was used as described as above until the point where the NMR standard should have been added. Instead, inside the glovebox, the catalyst was separated from the liquid by immobilizing the catalyst with a magnet. The liquid was collected and added to a vial with 1 mL of the 0.25 M dibenzyl ether standard. 0.5 mL of a new stock solution of ketone and silane (1 M and 1.2M, respectively) was

added and sealed with PTFE-lined screw cap again and placed in an aluminum-heating block as described above. This procedure was repeated for every recycle. The results are shown in Figure 4.

I. Test for heterogeneous catalysis

"Hot filtration test": A reaction was prepared as described in catalytic test, but was stopped after 12 h which corresponds to approximately 50% conversion. The mixture was taken into a glovebox, separated from the catalyst by a magnet, and filtered into a new 4 mL vial through a 0.22 µm syringe filter before the vial was sealed with a PTFE-lined screw cap. The vial was placed on an aluminum heating block at 90 °C for additional 8 hours. The mixture was analyzed as described earlier. The ¹H-NMR analysis showed completely inhibition of the catalytic activity.

Leaching test: Two experiments were prepared as described earlier and stopped after for 24h, however no NMRstandard was added to the mixture. Instead, the mixture was filtered to separate the catalyst from the liquid. The liquid was placed under vacuum to remove all volatile compounds. Afterwards, concentrated $HNO_3(65\% w/w)$ was added to the liquid, which was subsequently diluted to form a $2\% w/w HNO_3$ aqueous solution and filtered again before ICP analysis. (The mixture was clear and showed no sign of precipitation prior to the last filtration.) Both samples showed concentrations of metal below the blank and, evidently, metal leaching does not occur.



2. ZIF-67 characterization

Figure S1: Diffractogram of the synthesized ZIF-67 crystals.



Figure S2: TGA of ZIF-67 conducted in argon with a heating ramp of 5°C/min.

The synthesized ZIF-67 crystals are thermally stabile under argon atmosphere at temperatures below 500 $^{\circ}$ C, but at temperatures above 500 $^{\circ}$ C decomposition of the framework occurs, which results in a mass loss.



Figure S3: N₂-physisorption of ZIF-67 conducted at 77 K and degassed a room temperature 24 hours prior to the analysis.





Figure S4: SEM image of the synthesized ZIF-67 crystals

The synthesized ZIF-67 crystals are $600-900 \,\mu$ m in size evaluated from SEM images. The ZIF-67 crystals' characteristic rhombic dodecahedron shape is visible in the SEM image as well.

Characterization of the carbonized materials - Co@NC_{800} and CoNi@NC_x



Figure S5: Diffractograms of the synthesized catalysts - CoNi@NC₅₅₀, CoNi@₆₇₅, Co@NC₈₀₀, and CoNi@NC₈₀₀.



II. N₂-physisorption

Figure S6: N_2 -physisorption isotherms for the synthesized catalysts - CoNi@NC₅₅₀, CoNi@NC₆₇₅, Co@NC₈₀₀, and the CoNi@NC₈₀₀. The isotherm of CoNi@NC₈₀₀ is also presented in the article.

Element	Atomic %	weight $\%$
С	82.90%	65.24%
Co	3.29%	12.71%
Ni	3.30%	12.70%
Ν	6.48%	5.95%
Ο	3.24%	3.40%

XPS

III.

Figure S7: Atomic composition based on XPS analysis from CoNi@NC₈₀₀



Figure S8: 2p scan of cobalt in CoNi@NC₅₅₀, CoNi@NC₆₇₅, and Co@NC₈₀₀.

$\underbrace{\mathsf{Stop}}_{\mathsf{M}} = \underbrace{\mathsf{CoNi}_{\mathsf{M}}}_{\mathsf{M}} \underbrace{\mathsf{M}}_{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}}_{\mathsf{M}} \underbrace{\mathsf{M}}_{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}}_{\mathsf{M}} \underbrace{\mathsf{M}} \underbrace{\mathsf{M}}$

Ni 2p scan

Figure S9: 2p scan of nickel in CoNi@NC₅₅₀ and CoNi@NC₆₇₅.



Figure S10: 1s scan of nitrogen in CoNi@NC₅₅₀, CoNi@NC₆₇₅, Co@NC₈₀₀, and CoNi@NC₈₀₀.



Figure S11: 1s scan of carbon in CoNi@NC₅₅₀, CoNi@NC₆₇₅, Co@NC₈₀₀, and CoNi@NC₈₀₀.

IV. ICP

Sample preparation for ICP-OES analysis of CoNi@NC₈₀₀:

51.1 mgCoNi@NC was heated to 550 °C for 3h with a ramp of 5 °C/min under a hydrogen flow in a tube furnace. The resulting black powder was dissolved in 65% (w/w) HNO₃, diluted 250 times and filtered before ICP analysis was conducted. The resulting concentration of metal was between 0.5-1 ppm in 2% HNO₃. In Figure S12 the calibration curves used to measure the Co and Ni are presented.

In Table S1 with the corresponding measured concentrations of Co and Ni together with the leaching test described earlier.

Table S1: ICP results of the catalysts $CoNi@NC_{800}$ and two leaching test under optimized conditions.

	Co conc. (ppm)	Ni conc. (ppm)	Co:Ni	[M] w/w
CoNi@NC ₈₀₀	0.815	0.540	60:40	66.4 %
Leaching test 1	≤ blank	≤ blank		
Leaching test 2	≤ blank	≤ blank		





Figure S12: Calibration curves for Co and Ni





Figure S13: SEM images of CoNi@NC₈₀₀



Figure S14: SEM image of ZIF-67 carbonized at 800 °C without introducing nickel to the pores

SEM image of carbonized ZIF-67 without the introduction of $Ni(NO_3)_2$ to the pores prior to the carbonization. It can be seen that the rhombic dodecahedron shape is preserved.

3. Hydrosilylation of ketones

I. Optimization of reaction conditions

Table S2: Optimization in heptane

0.5 m	0 10 mg CoN 1.2 equiv N heptane (1M) nmol	Ni@NC ₈₀₀ O Me ₂ PhSiH , 90 °C, 24 h	SiMe ₂ Ph
Entry	conditions	Conversion (%)	Yield (%)
1	-	100	100
2	5 mg catalyst	64	60
3	7.5 mg catalyst	75	73
4	in air	97	97
5	70 °C	60	44
6	no catalyst	2	0
7	no silane	0	0
8	solvent=toluene	81	81

Table S3: Optimization in toluene



II. Recycling



Figure S15: TEM image of the catalyst after the sixth recycle

The TEM image clearly shows how the distributed nanoparticles have agglomerated into a big lump of metal, which evidently cause a deactivation of the catalyst.

4. References

1 H. Hu, B. Guan, B. Xia and X. W. Lou, J. Am. Chem. Soc., 2015, **137**, 5590-5595.