Electronic Supplementary Information

Palladium nanoparticles supported on a nickel pyrazolate metal organic framework as catalyst for Suzuki and carbonylative Suzuki couplings

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1. Experimental section

1.1. Materials and methods

All materials including solvents were obtained from commercial sources, were of reagent grade and were used without further purification. Infrared **(IR)** spectra were acquired in transmission mode on a Bruker 113v FTIR spectrometer. Thermogravimetric analyses **(TGA)** were performed, under either nitrogen or a reactive air atmosphere, on a TG-DTA *Setaram* SETSYS 16/18 equipment, at a heating rate of 20 °C min^{-1}. X-ray Powder Diffraction Structural Analysis (**XRPD**): except for the structural analysis, all the X-ray powder diffraction data were acquired on a D8 ADVANCE Bruker AXS diffractometer using CuKα radiation (λ = 1.5418 Å). **Gas Adsorption Measurements** conventional adsorption isotherms were measured using a Micromeritics ASAP 2020 HD volumetric instrument under continuous adsorption conditions. Brunauer– Emmet–Teller (BET) analyses were carried out to determine the total specific surface areas for the N_2 isotherms at 77 K. **GC-FID and GC/MS** Spectra of the organic products were obtained using the HP 5890 (Hewlett Packard) instrument with mass detector 5971 A. Capillary column HP 5 was used with a non-polar liquid phase containing 95% of dimethyl- and 5% of diphenylpolysiloxane. **ICP** measurements of the palladium content were performed using spectrometer ARL model 3410.

TEM measurements were performed using a FEI Tecnai G^2 20 X-TWIN electron microscope with LaB_6 catode providing 0.25 nm resolution. To the small sample of catalyst 2 mL of methanol were added and the resulted mixture was ultrasonically treated for 5 min. Specimens for TEM studies were prepared by putting a droplet of a colloidal suspension on a copper microscope grid followed by evaporating the solvent under IR lamp for 15 min. X-ray photoelectron spectra (**XPS**) were conducted on a Kratos Axis Ultra-DLD X-ray photoelectron spectrometer equipped with Al Kα radiation (1486.6 eV)

1.2. Synthesis of MOF [Ni(H₂BDP-SO₃)₂] [1]

The $[Ni(H_2BDP\text{-}SO_3)_2]$ was prepared as described in the literature. $H_2BDP\text{-}SO_3H$ (0.050 g, 0.172 mmol) was dissolved in DMSO (3 mL) in a 50 mL Schlenk flask, and DMF (3 mL) was added to this solution. The mixture was heated to 60 °C, and $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.085 g, 0.5 mmol) was added under stirring. The mixture was then allowed to react for 5 h at 160 °C. After being cooled at room temperature, the yellowish solid was collected by filtration, washed with DMF (3 × 10 mL), and dried under vacuum.

1.3. Synthesis of Pd@[NiH₂BDP-SO₃]

In a typical synthesis, 0.050 mg $[PdCl_2(CH_3CN)_2]$ were added into 15.0 mL of methanol. After addition of 0.080 mg activated $[Ni(H_2BDP\text{-}SO_3)_2]$. After 1 day, the solid was filtered and washed with methanol to remove the unreacted $[PdCl_2(CH_3CN)_2]$. Was obtained as a dark red color powder, which was kept under air atmosphere.

1.4. Suzuki cross coupling reaction

In a typical reaction, a mixture of aryl halides (1 mmol), arylboronic acid (1.2 mmol), base (1.5 mmol), and the catalyst (0.39 mg, 0.005 mmol of Pd against aryl halide substrate) in solvent (5 mL) was placed in a glass vial flask. The resulting mixture was stirred for 0.5-20 h at 25-100 °C. After the reaction was complete, the mixture was cooled to room temperature

and the catalyst was filtered off. Next, the organic products were separated by extraction with 10 mL of diethyl ether. The extracts (10 mL) were GC-FID analyzed with dodecane (0.050 mL) as an internal standard to determine the conversion of aryl halide. The products of the reaction were determined by GC–MS.

1.5. Carbonylative Suzuki–Miyaura reaction

Reactions were performed in a Schlenk tube. Weighted amounts of the solid reactants: phenylboronic acids (1.1 mmol), base (3.0 mmol), catalyst (0.39 mg), 4-iodoanisole (1 mmol), and 5 mL of solvent (anisole or toluene) were introduced to the Schlenk tube. Next, the Schlenk tube was sealed with a teflon septum equipped with capillary connected to a CO gas cylinder with CO and introduced into an oil bath preheated to 100 °C. The continuous flow of gas (aprox. 0.5 L/h) was made possible by the use of a fine needle inserted in the septum. The reaction mixture was magnetically stirred at a given temperature for 5 h, and after this time it was left for several minutes to cool down. The organic product was separated by extraction with 10 mL of diethyl ether. The extracts (10 mL) were GC-FID analyzed with dodecane (0.050 mL) as an internal standard to determine the conversion of aryl iodide. The products of the reaction were determined by GC–MS.

Table S1. Optimization of the reaction condition[a]

Entry	Base	Solvent	Conversion (%)[b]
1	K_2CO_3	$^iPrOH/H_2O$[e]	0[c]
2	K_2CO_3	$^iPrOH/H_2O$[e]	0[d]
3	K_2CO_3	H_2O	50
4	K_2CO_3	^iPrOH	60
5	K_2CO_3	$^iPrOH/H_2O$[e]	91[f], 97[g]
6	K_2CO_3	$^iPrOH/H_2O$[e]	58[h]
7	K_2CO_3	$^iPrOH/H_2O$[e]	0[i]

a) Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), base (1.5 mmol), Pd@[Ni(H$_2$BDP-SO$_3$)$_2$] (0.5 mol % of Pd) solvent (H$_2$O/^{i}PrOH) (5 mL).

b) GC analysis, conversion based on 4-bromoanisole.

c) Without catalyst.

d) [Ni(H$_2$BDP-SO$_3$)$_2$] (alone).

e) 1:1 (v/v) ratio.

f) 25 °C, 8 hours

g) 60 °C, 4 hours

h) Pd@[Ni(H$_2$BDP-SO$_3$)$_2$] (0.3 mol % of Pd)

i) Control leaching reaction, ICP of the liquid phase is 0,039 ppm of Pd

Table S2. Optimization of the reaction condition[a]
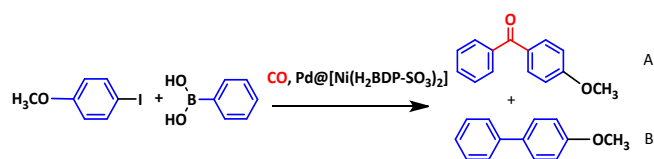
Entry	Base	Solvent	Time (h)	Temp. (°C)	Conv.(%)[b]	A (%)	B (%)
1	K_2CO_3	Toluene	5	105	30*c	12	18
2	K_2CO_3	Anisole	5	105	80*c	21	59
3	K_2CO_3	Anisole	5	105	66*d	51	15
4	K_2CO_3	Anisole	1	105	42*e	42	0
5	K_2CO_3	Anisole	2	105	42*e	42	0
6	K_2CO_3	Anisole	3	105	49*e	49	0
7	K_2CO_3	Anisole	5	105	50*e	50	0
8	K_2CO_3	Anisole	16	105	67*e	67	0
9	K_2CO_3	Anisole	3	80	33*e	33	0
10	$KHCO_3$	Anisole	3	80	32*e	32	0
11	KOH	Anisole	3	80	27*e	27	0
12	K_2CO_3	Anisole	7	80	34*e	34	0
13	K_2CO_3	DMF	3	80	0*e	0	0
14	K_2CO_3	Anisole	3	80	36**e	36	0
15	K_2CO_3	Anisole	3	105	58**e	58	0
16	K_2CO_3	Anisole	3	105	61***e	61	0

a) Reaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.1 mmol), base (3 mmol), solvent (5 mL).
b) GC analysis, conversion based on 4-iodoanisole.
c) balloon
d) 5 Bar
e) 10 Bar

* 0.5 % mol Pd
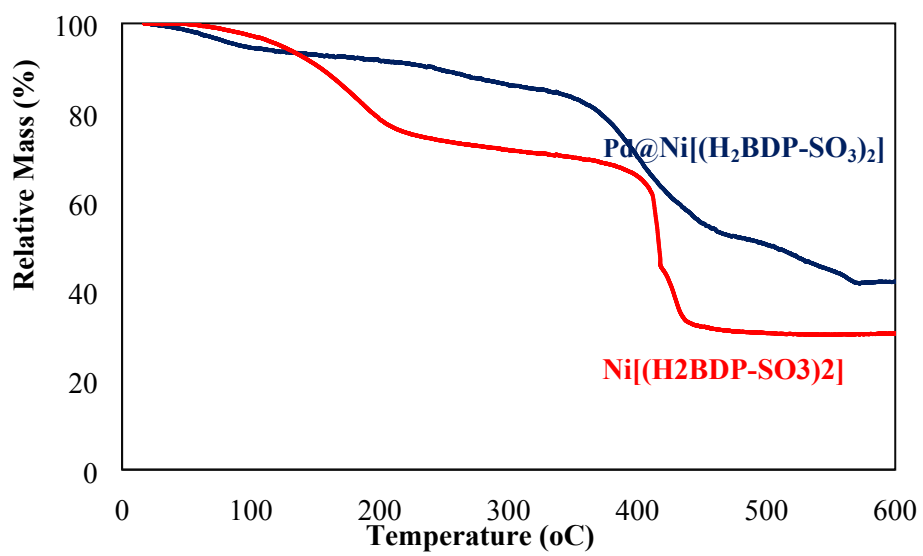** 1 % mol Pd
*** 2 % mol Pd

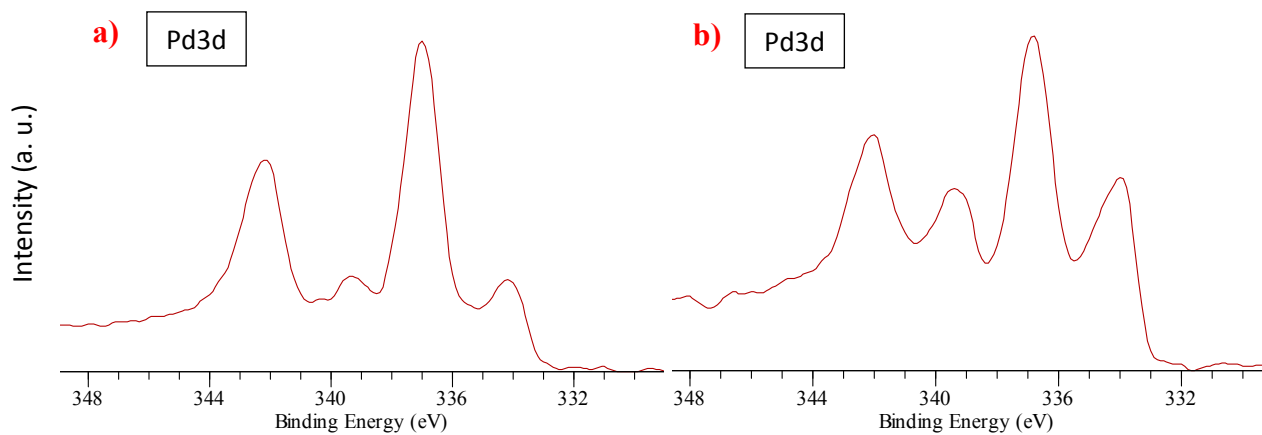Fig. S1. TGA curves of (blue) Pd@[Ni(H$_2$BDP-SO$_3$)$_2$] and (red) [Ni(H$_2$BDP-SO$_3$)$_2$].

Fig. S2. XPS spectrum of different elements of Pd@[Ni(H$_2$BDP-SO$_3$)$_2$]: a) before reaction, b) after reaction. Pd form: Pd(0) 334.0 and 339.3 eV, Pd(II) 336.9 and 342.6 eV.
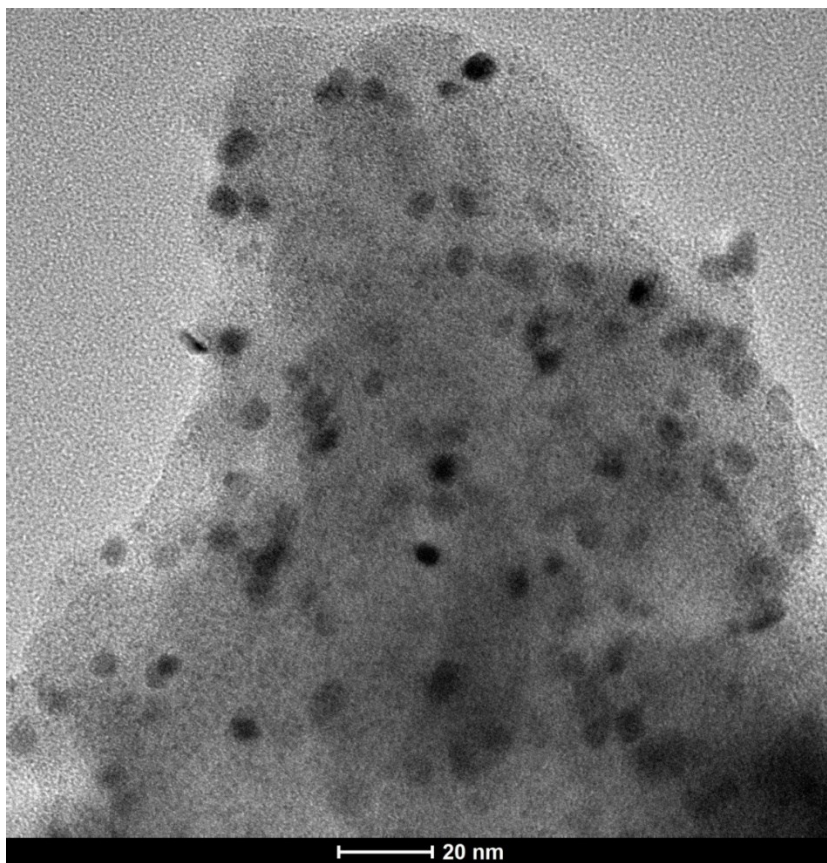
Fig. S3. TEM images of Pd@[Ni(H$_2$BDP-SO$_3$)$_2$] after Suzuki reaction 4st run.
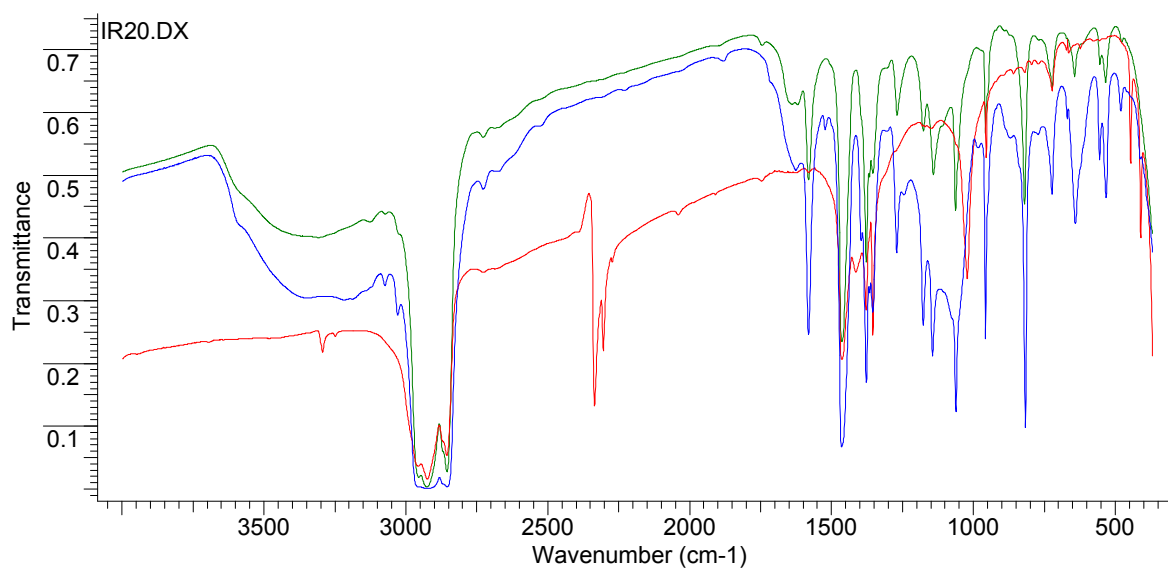
Fig. S4. FT-IR (nujol) spectra of: **[PdCl₂(CH₃CN)₂]** (red), **[Ni(H₂BDP-SO₃)₂]** (blue) **Pd@[Ni(H₂BDP-SO₃)₂]** (green)

References

1 V. Colombo, C. Montoro, A. Maspero, N. Masciocchi, S. Galli, E. Barea and J.A.R. Navarro, *J. Am. Chem. Soc.*, 2012, **134**, 12830.