

Electronic Supplementary Information

Hydroxyapatite supported palladium catalysts for Suzuki-Miyaura cross-coupling reaction in aqueous medium

Arindam Indra,^a Chinnakonda S. Gopinath,^b Sumit Bhaduri,*^a and Goutam Kumar Lahiri*^a

^a*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in (GKL), sbhaduri@chem.iitb.ac.in (SB)*

^b*Catalysis Division, National Chemical Laboratory, Pune-411008, India*

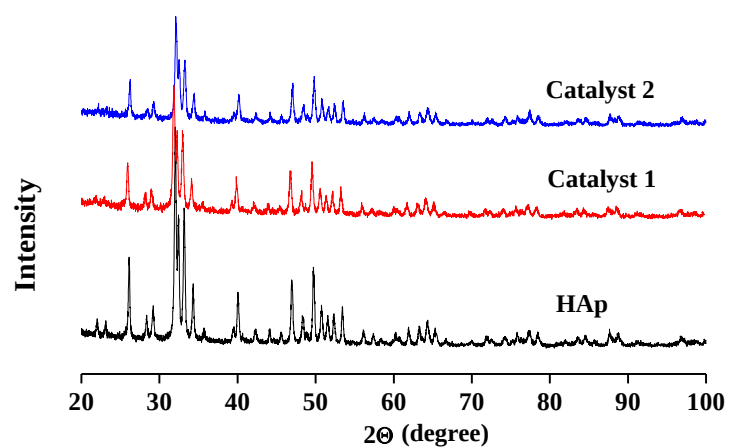


Fig. S1. Powder X-ray diffraction patterns of the catalysts **1**, **2** and hydroxyapatite.

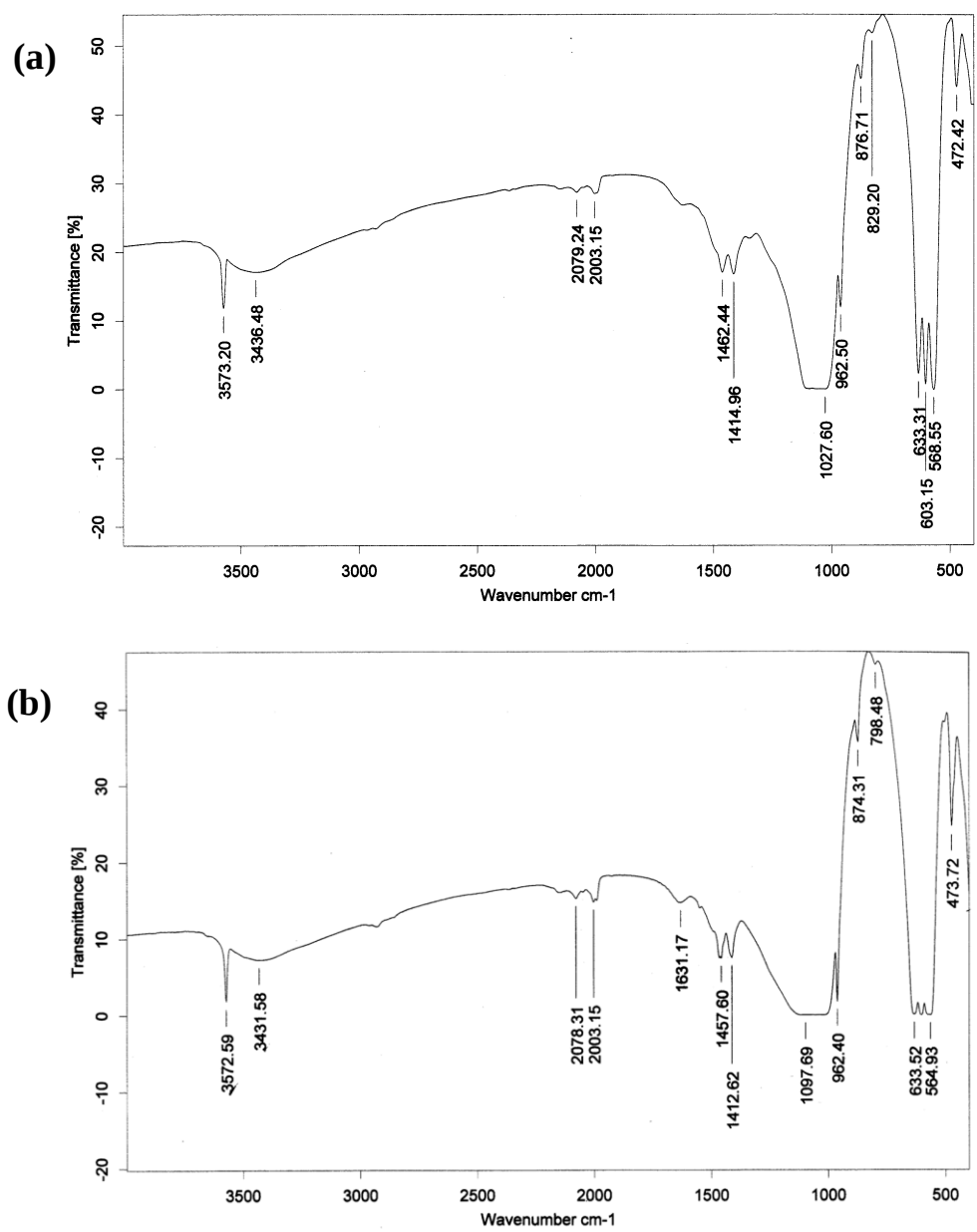


Fig. S4. Attenuated total reflectance (ATR) IR spectra of (a) hydroxyapatite and (b) catalyst 1.

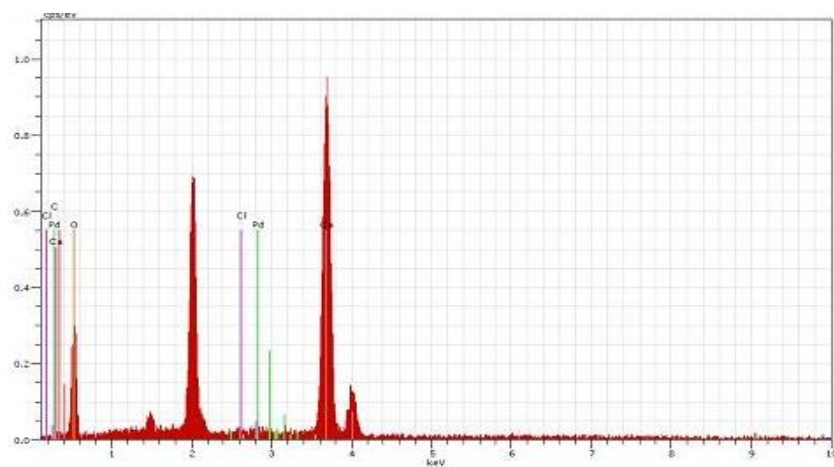


Fig. S3. EDX spectrum of fresh catalyst **1**.

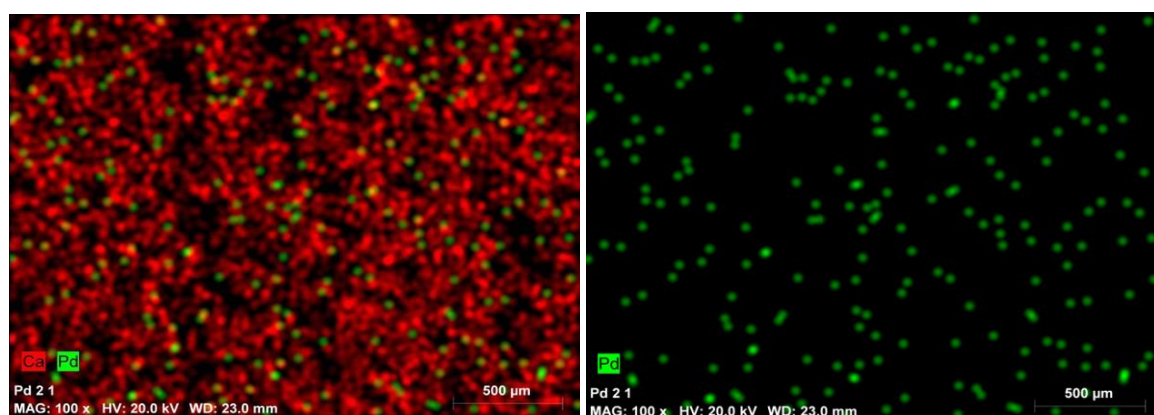


Fig. S4. X-ray mapping of fresh catalyst **1** showing the distribution of palladium (green) and calcium (red) on the surface.

Table S1 Optimization of the reaction conditions with catalysts **1** and **2**^a

Entry	ArB(OH) ₂	Ar'-X	Cat.	Solvent	Base	TON ^b	Hetero-coupled product selectivity ^c
1	4-MePhB(OH) ₂	PhI	1	Toluene	K ₂ CO ₃	2941	97
2	4-MePhB(OH) ₂	PhI	2	Toluene	K ₂ CO ₃	647	95
3	4-MePhB(OH) ₂	PhI	1	H ₂ O	K ₂ CO ₃	911	92
4	4-MePhB(OH) ₂	PhI	2	H ₂ O	K ₂ CO ₃	176	91
5	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	K ₂ CO ₃	2941	97
6	4-MePhB(OH) ₂	PhI	2	H ₂ O/TBAB	K ₂ CO ₃	559	96
7	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	Na ₂ CO ₃	2853	96
8	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	Cs ₂ CO ₃	2764	92
9	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	BaCO ₃	2825	95
10	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	NaOAc	2825	98
11	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	NaF	1497	98
12	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	NaOH	1723	72
13	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	NEt ₃	1921	90
14	4-MePhB(OH) ₂	PhI	1	H ₂ O/TBAB	-	904	99
15	PhB(OH) ₂	4-COCH ₃ PhBr	1	Toluene	K ₂ CO ₃	2720	97
16	PhB(OH) ₂	4-COCH ₃ PhBr	2	Toluene	K ₂ CO ₃	412	91
17	PhB(OH) ₂	4-COCH ₃ PhBr	1	H ₂ O/TBAB	K ₂ CO ₃	2666	96
18	PhB(OH) ₂	4-COCH ₃ PhBr	2	H ₂ O/TBAB	K ₂ CO ₃	382	94

^aReaction conditions: The catalytic reactions were carried out with 0.5 mmol aryl halide, 0.6 mmol aryl boronic acid, 1.5 mmol of base, 1.7X10⁻⁴ mmol Pd as catalyst **1** or **2**, 5 mL solvent at 353 K for 24 h in atmospheric condition. 0.5 mmol TBAB was added in water where mentioned.

^bYield was determined by GC and TON was calculated from GC yield.

^cDetermined by GC.