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Advanced heterogeneous Pd catalysts for the Suzuki-Miyaura reaction with aryl bromides

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S1. Experimental

S1.1. General

All reactants and solvents were obtained from Sigma-Aldrich or Acros (grade p.a.) and were used as received without further purification or drying. The quantitative compositions of the samples were determined using gas chromatography (GC) (Chromatec Crystal 5000.2 instrument fitted with a flame ionization detector [FID] and 15-m HP-5 methyl phenyl siloxane capillary column) at a 1/10 split ratio, nitrogen as carrier gas, column temperature 110-250ºC; injector and detector temperatures 200ºC. Samples for GC analysis were collected using a syringe with a steel needle at different reaction time points. The concentrations of the reaction products were determined by GC using the Chromatec Analytic 3.0 software with an internal standard method using preliminary plotted calibration curves. To estimate the reproducibility of the data, each experiment was performed three times.

The determined by GC concentrations of the reaction products were used to calculate TOF and TON values, and to plot phase trajectories (see Section S2). For the plotted phase trajectories, the appropriate polynomial fitting of the experimental data was used in order to be convinced in the overlapping/changing phase trajectories.

S1.2. Catalyst preparation.

2.3Pd/SiO_2-IL

Perlkat-97-0 Silica Gel was modified by 3-chloropropyltrimethoxysilane according to the described standard method.[S1,S2] The next stage of quaternization of *N*-ethylimidazole with chloropropyl fragments grafted to the surface was carried out in an evacuated ampoule at 180°C for 12 h, and then the silica gel modified with ionic liquid (SiO_2-IL) was washed with ethanol to remove excess reagents. The reaction with palladium chloride (0.5 g per 10 g of SiO_2-IL) proceeded in a mixture of acetone and acetonitrile with slight heating on a magnetic stirrer until

the solution became colorless (24 h) as was described.[S3] After decantation and washing the resulting 2.3Pd/SiO_2-IL contained 2.3 wt %Pd, 4.1wt %N, and 3.3wt %Cl.

0.1- and 0.05Pd/Al_2O_3-Imp

Two samples with 0.1 and 0.05 wt % Pd were prepared by impregnating γ-Al_2O_3 (AOK-63-11, B, 0.4–1 mm granules) with $Pd(NO_3)_2$ with the following treatment for 3 h at 300°C in air and then for 2 h at 400°C in hydrogen according to a procedure similar to the previous study.[S3]

0.03Pd/Al_2O_3-LED

Laser electrodispersion (LED) was used for the loading Pd nanoparticles on the outer surface of γ-Al_2O_3 granules under the action of laser radiation on Pd target in vacuum.[S4,S5] In accordance with the previous data,[S5] the content of Pd loaded during 4 min was 0.03 wt %.

Reference catalyst **4Pd/C** was prepared using $Pd(OAc)_2$ at a Pd loading of 4 wt %. The support mesoporous carbon material ('Sibunit',[S6] 0.16-0.25 mm, 1 g) was suspended in toluene (20 ml). $Pd(OAc)_2$ was added, and the suspension was stirred at 95°C for 30 min. Completeness of $Pd(OAc)_2$ adsorption was controlled by observing changes in the intensity of the absorption band in solution at 300 nm. Then, formic acid (0.04 ml) was added to reduce palladium on the carbon surface, and the suspension was stirred for 20 min until discoloration occurred. The resulting catalyst was filtered and washed with acetone. The catalysts were used after drying in a vacuum.

S1.3. Catalyst characterization

Amount of metal in the synthesized Pd precursors were measured by Atomic absorption spectroscopy (AAS) using ThermoiCE 3000 (Thermo Fisher Scientific Inc., USA). Microphotographs of the samples before and after catalysis were obtained via scanning and transmission electron microscopy (SEM and TEM) on JEOL JSM 6000 NeoScope and JEOL JEM 2100F/UHR instruments with a resolution of 0.1 nm, respectively. For TEM study, the granules were exposed to ultrasonic treatment in alcohol as in the previous study.[S3] A qualitative analysis of the surface was performed in situ by means of energy dispersive analysis (EDA) using a JED-2300 instrument. X-ray photoelectron spectra were recorded on an Axis Ultra DLD spectrometer (Kratos) equipped with a monochromatic AlKα radiation source with a neutralizer. High-resolution spectra were recorded at analyzer transmission energy and 40 eV. Calibration was performed using the binding energies of Al 2p (74.2 eV) and Si 2p (103.6 eV) spectra. Pd $3d_{5/2}$ spectra were fitted by three components corresponding to Pd^0 (335.5 eV), PdO (336.7 eV) and Pd^{2+} (a doublet with the binding energy of 338.4 eV).

S1.4. Suzuki-Miyaura reaction

Competing 4-bromoacetophenone and bromobenzene (5 mmol each), and naphthalene (GC internal standard, 1 mmol) were dissolved in non-anhydrous DMF (5 ml). The solution was placed in a 25 ml one-necked round bottom flask equipped with a magnetic stir bar and a septum inlet containing phenylboronic acid (5 mmol), NaOAc (6.5 mmol) as the base, and Pd precursor ($5.6 \cdot 10^{-4}$ – 0.8 μmol of Pd, $1.12 \cdot 10^{-5}$ – $1.6 \cdot 10^{-2}$ mol.%) under air. The reaction was initiated by placing the reactor in a pre-heated oil bath (140ºC) with stirring (480 rpm). The reaction was carried out for 7–8 h.

A weight balance was calculated for each reaction sample as the amounts of aryl bromides consumed and biaryls formed. A deviation did not exceed 5%. A weight balance indicated that in the reaction between unsubstituted bromobenzene and phenylboronic acid biphenyl formed exclusively in cross-coupling reaction without detectable outcome from oxidative homocoupling of phenylboronic acid or reductive homocoupling of bromobenzene.

S2. Catalytic performance and phase trajectories of the Suzuki-Miyaura reaction with two competing aryl bromides.

Table S1. Performance of the synthesized Pd catalysts and reference homogeneous ($PdCl_2$) and heterogeneous (4Pd/C) catalysts in competitive Suzuki-Miyaura reaction with two aryl bromides (Section S1.4) at Pd loading 0.8 μmol.

Catalyst sample	TOF, min^{-1}	TON
$0.03Pd/Al_2O_3$ –LED	210	1860
$0.1Pd/Al_2O_3$ – Imp	220	2850
$0.05Pd/Al_2O_3$ – Imp	400	3600
$2.3Pd/SiO_2$ – IL	650	2600
4Pd/C	140	1700
$PdCl_2$	290	1800

The data on the concentrations of biaryls formed from competing aryl bromides (Section S1.4) were used to plot phase trajectories for the experiments with different Pd precursors. The concentration of biphenyl (product of the Suzuki-Miyaura reaction between bromobenzene and phenylboronic acid) is shown along Y axis, and the concentration of 4-acetylbiphenyl (product of the reaction between 4-bromoacetophenone and phenylboronic acid) is shown along X axis. Therefore, tangent slope to any point of a trajectory is the ratio d[Ph-Ph]/d[4-MeC(O)C_6H_4-Ph], *i.e.*, the ratio of the formation rates of the products from competing reactions.

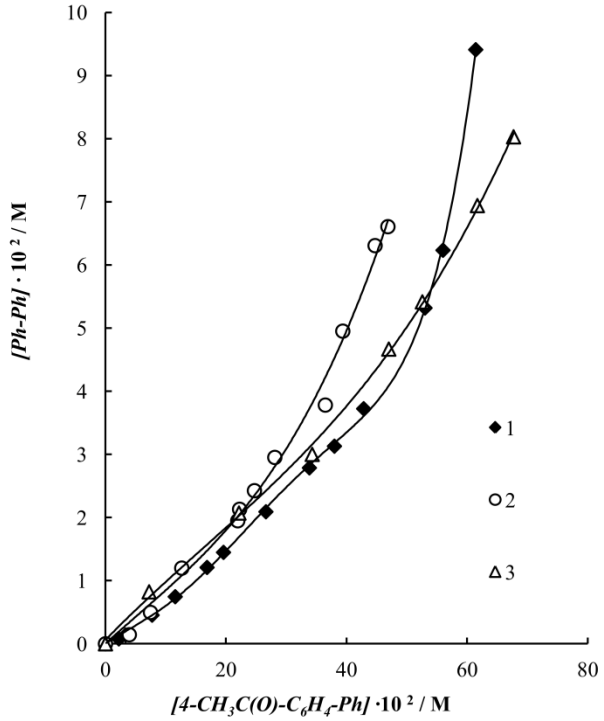

Figure S1. Phase trajectories of Suzuki-Miyaura reaction with competing bromobenzene and 4-bromoacetophenone (Section S1.4) while varying the nature of Pd precursor with total Pd loading 8 μmol: (1) 2.3Pd/SiO_2 – IL, (2) 4Pd/C, (3) $PdCl_2$.

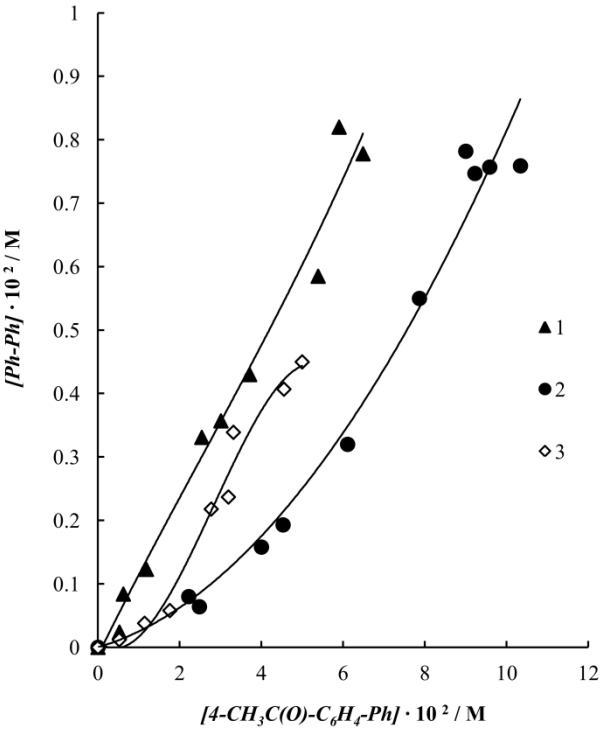

Figure S2. Phase trajectories of Suzuki-Miyaura reaction with competing bromobenzene and 4-bromoacetophenone (Section S1.4) while varying the nature of Pd precursor with total Pd loading 0.08 μmol: (1) 0.05Pd/Al_2O_3 – Imp, (2) 0.1Pd/Al_2O_3 – Imp, (3) 0.03Pd/Al_2O_3 –LED.

S3. Catalysts structure

Table S2. Content of Si, Pd and Cl on the surface of fresh and spent 2.3Pd/SiO_2-IL according to SEM-EDA.

Element	E, keV	atom%	
		fresh	spent
Si	1.739	12.84	10.28
Pd	2.838	0.14	0.09
Cl	2.621	0.80	0.20

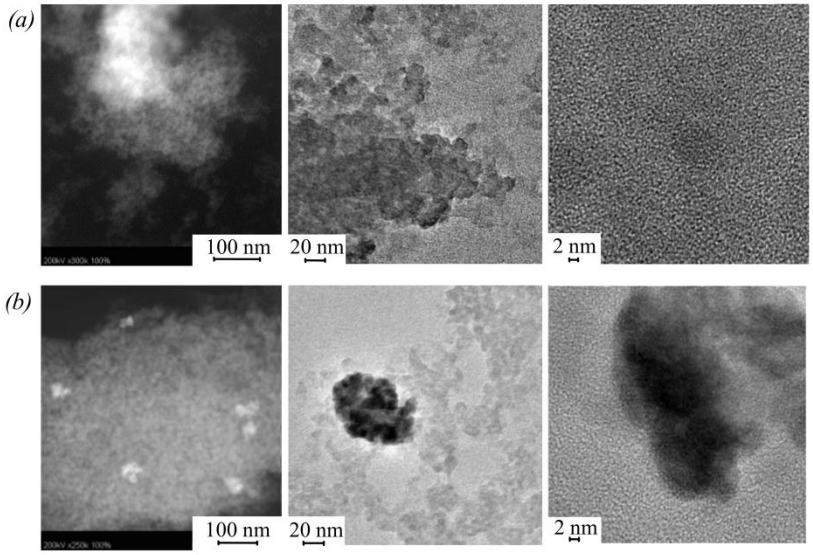

Figure S3. TEM images of fresh (a) and spent (b) 2.3Pd/SiO_2-IL.

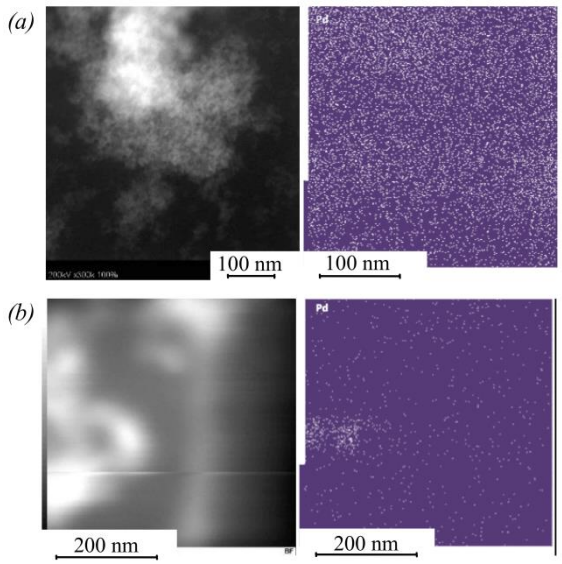

Figure S4. TEM images and EDA Pd mapping of fresh (a) and spent (b) 2.3Pd/SiO_2-IL.

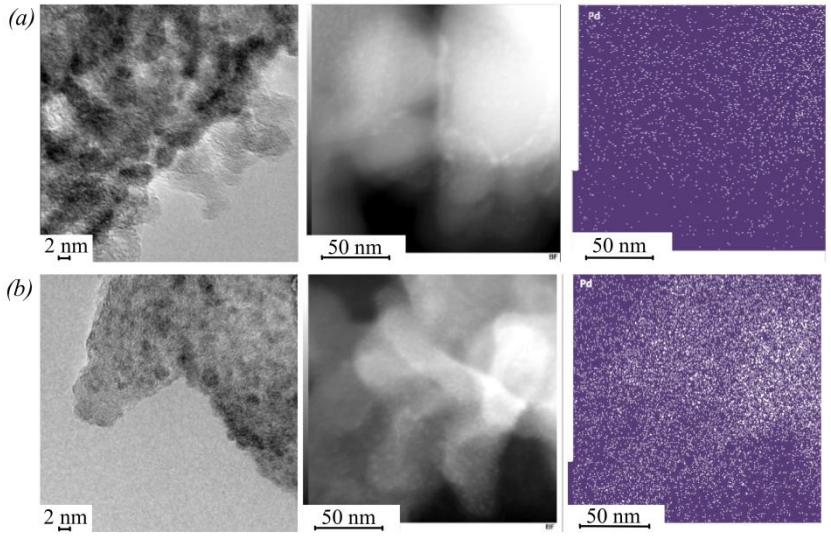

Figure S5. TEM images and EDA Pd mapping of fresh (a) and spent (b) 0.03Pd/Al_2O_3-LED.

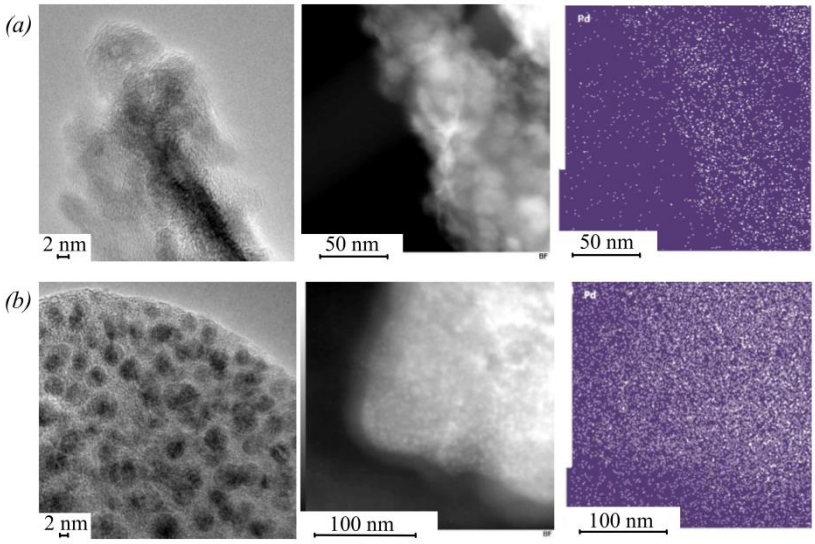

Figure S6. TEM images and EDA Pd mapping of fresh (a) and spent (b) 0.1Pd/Al_2O_3-Imp.

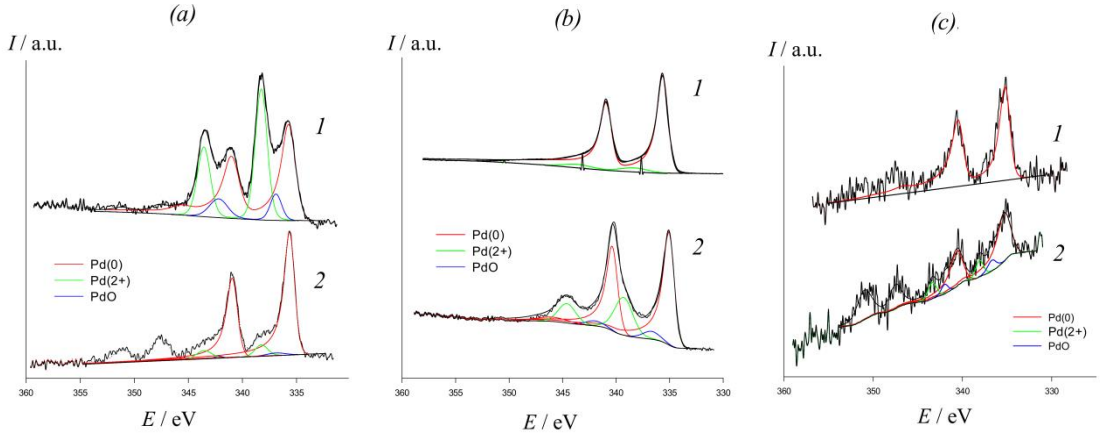

Figure S7. Pd3d XPS spectra of fresh (1) and spent (2) 2.3Pd/SiO_2-IL (a), 0.03Pd/Al_2O_3-LED (b), and 0.1Pd/Al_2O_3-Imp (c).

Table S3. Fraction of palladium atoms in different oxidation states on the surface of fresh[S5] and spent 2.3Pd/SiO_2-IL, 0.03Pd/Al_2O_3-LED and 0.1Pd/Al_2O_3-Imp according to XPS data.

Sample		ν (Pd), atom % (E_b, eV)		
		Pd^0 (335.5)	PdO (336.7)	Pd^{II} (338.4)
2.3Pd/SiO_2-IL	fresh	58	9	33
	spent	90	-	10
0.03Pd/Al_2O_3 –LED	fresh	94	-	6
	spent	77	4	19
0.1Pd/Al_2O_3-Imp	fresh	100	-	-
	spent	85	5	10

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