Palladium Nanoparticles on Graphite Oxide and Its Functionalized Graphene Derivatives as Highly Active Catalysts for the Suzuki-Miyaura Coupling Reaction

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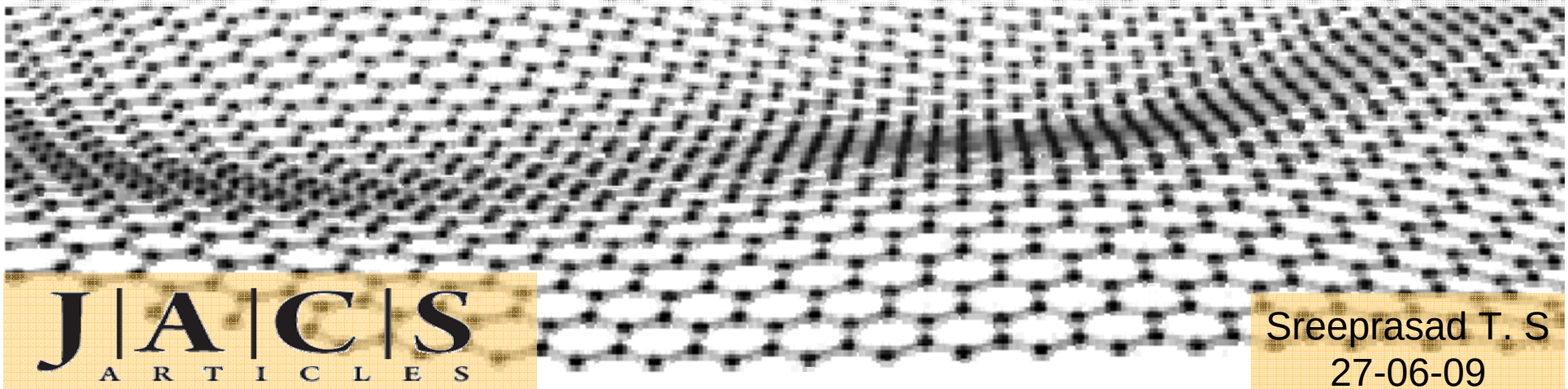


J|A|C|S ARTICLES

Sreeprasad T. S
27-06-09

Introduction

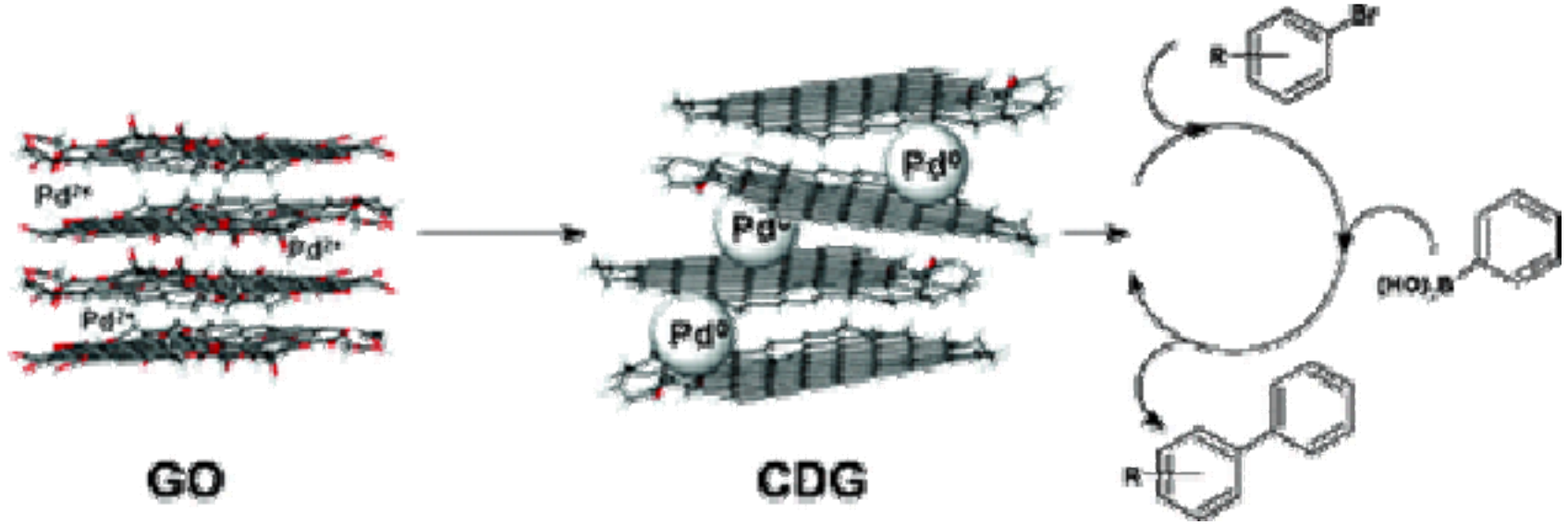
- *Carbon based nanomaterials :*
  Graphite Oxide (GO) and Chemically Derivatized graphene (CDG)
- *GO and CDG*
  - *Easily available by controlled chemical or electrochemical oxidation of graphite*
  - *The sorption and intercalation of ions and molecules is possible.*
  - *High specific surface area of GO and CDG of 400 $m^2 g^{-1}$ up to 1500 $m^2 g^{-1}$*

Few examples of GO-based materials as catalysts

1) *USSR patent, Titelman et al. - deposition of NiO and CuO by thermal reduction of metal amine precursors on a GO support as a catalyst for removing oxygen impurities from industrial gases.*
2) *Kyotani et al. synthesized carbon-metal composites by thermal treatment of Na^+, Ca^{2+}, Cu^{2+}, and Fe^{2+}-exchanged graphite oxide.*
3) *Kovtyukhova and co-workers investigated the intercalation of different transition-metal complexes in GO.*
4) *Mastalir et al. were the first to determine the high catalytic activity and selectivity of their nano-Pd/GO systems in liquid-phase hydrogenation of alkynes.*

Pd nanoparticles- catalysts for C-C coupling reactions.

Present study, exploit GO and its CDG derivatives as a support for palladium clusters and nanoparticles. The Suzuki-Miyaura reaction has been selected as model reaction for evaluating GO- and CDG-based palladium catalysts.



$$R_1{-}BY_2 + R_2{-}X \xrightarrow[\text{Base}]{\text{Pd catalyst}} R_1{-}R_2$$

Experimental

Preparation of GO

GO was prepared by oxidation of graphite flakes *according* to the method escribed by Hummers and Offemann. The product -Freeze-dryed -dark brown solid - was carefully powdered in a ball mill (60-*μm mesh) with cooling.*

Ion -exchange with Pd

2.5g GO was dispersed in 200 mL water - palladium acetate (1.1 mM) was added and sonicated for 5 mns. Kept for cation exchange overnight. Washed several times with water and acetone - Pd^{2+}-GO was dried in at 40 °C and gently powdered through a 150-*μm mesh.* Pd content amounted to 3.4%.

The generation of Pd^0 nanoparticles within the GO support (Pd^0-CDG-H_2)

Hydrogen was bubbled through a suspension of Pd^{2+}-GO (0.5 g) in ethanol (100 mL) for 45 min with a flow of 40 mL min^{-1}. After evaporation of the solvent, the obtained material was again powdered through a 150-*μm mesh.*

Partial reduction of Pd^{2+}-GO with hydrazine hydrate (Pd^0-CDG-N_2H_4)

0.16 mL (3.3 mmol) of hydrazine hydrate (99.9% N_2H_5OH) was added to a suspension of Pd^{2+}-GO (0.2 g) in water (50 mL). Stirred overnight, the grayish slurry centrifuged and washed with water several times. The residue was then dried at 40 °C and gently powdered through a 150-*μm mesh.*

Preparation of Pd^0-CDG-EXP

Placing Pd^{2+}-GO (0.5 g) in a Schlenck tube under an argon atmosphere and heating the material with a Bunsen burner to 500-600 °C for 2 min.

Procedure for the Kinetic Measurements.

The reaction vessels were charged with palladium catalyst (x μmol) sodium carbonate (106 mg, 1 mmol, 2 equiv), boronic acid (0.55 mmol), and aryl bromide (0.50 mmol). After automatic addition to each vessel of ethanol (2 mL) and water (2 mL), the mixtures were shaken (600 min^{-1}) at rt. After 10, 30, 60, 120, 180, 240, 300, 360, 420, and 1440 min, small probes (20 μL) were taken and given in HPLC vessels with acetonitril (950 μL + 30 μL acetic acid). From these probes, the conversion was calculated via HPLC.

Procedure for the Suzuki Reaction.

A pressure tube was charged with boronic acid (0.55 mmol), sodium carbonate (106 mg, 1 mmol), aryl bromide (0.5 mmol), and palladium catalyst 2 (4.0 mg). Ethanol (2 mL) and water (2 mL) were added, and the flask was sealed with a Teflon screw cap and stirred in a preheated oil bath (80 °C) for the time indicated, followed by taking 10 *μL of the* mixture for HPLC analysis.

Results and Discussion
Synthesis and Characterization of the CDG Catalysts.

Table 1. Catalysts Investigated in the Suzuki–Miyaura Coupling Reaction Including Conventional Pd/C **1** as Benchmark

sample	composition[a]	oxygen content[b] (wt %)	Pd loading[c] (wt %)	particle diameter[d] (nm)	surface area MB[e] ($m^2\ g^{-1}$)	surface area BET[f] ($m^2\ g^{-1}$)
Pd/C **1**[g]		n.d.	10	n.d.	n.d.	820
Pd^{2+}-GO **2**	$C_6H_{1.9}O_{3.2}$	41	3.4	4 ± 1[h]	1050 (430)	n.d.
Pd^0-CDG-H_2 **3**	$C_6H_{0.9}O_{1.7}$	28	3.4	7 ± 2	350 (250)	n.d.
Pd^0-CDG-N_2H_4 **4**	$C_6H_{1.2}O_{1.5}$	25	3.5	54 ± 28	410 (130)	220
Pd^0-CDG-EXP **5**	$C_6H_{0.5}O_{1.1}$	19	6.0	3 ± 1	890 (410)	650

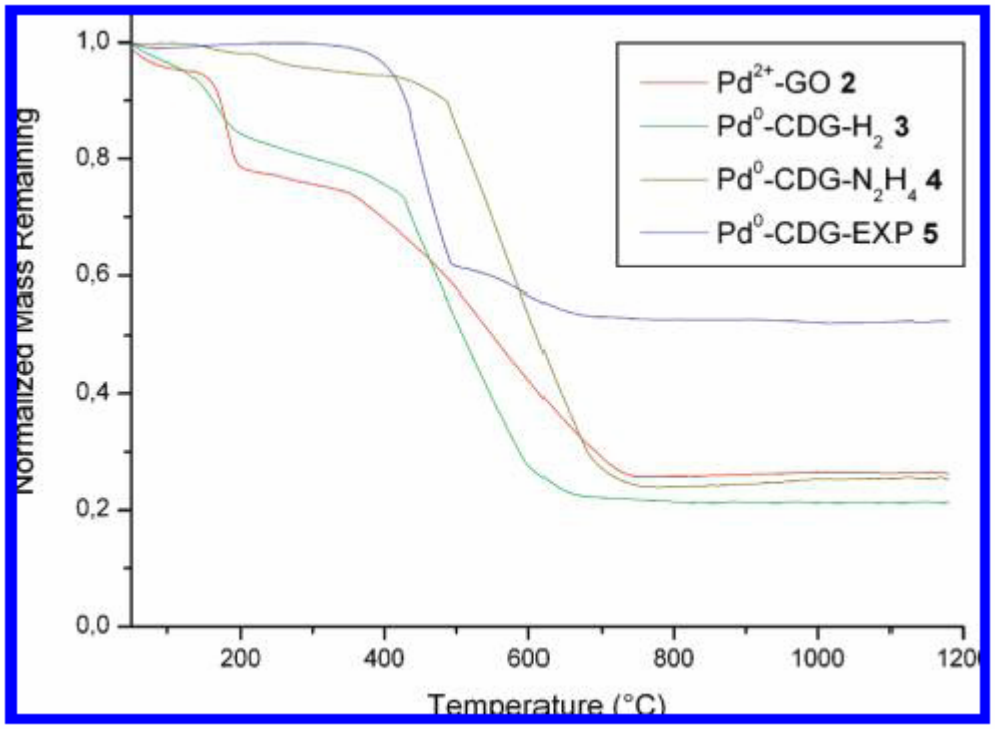
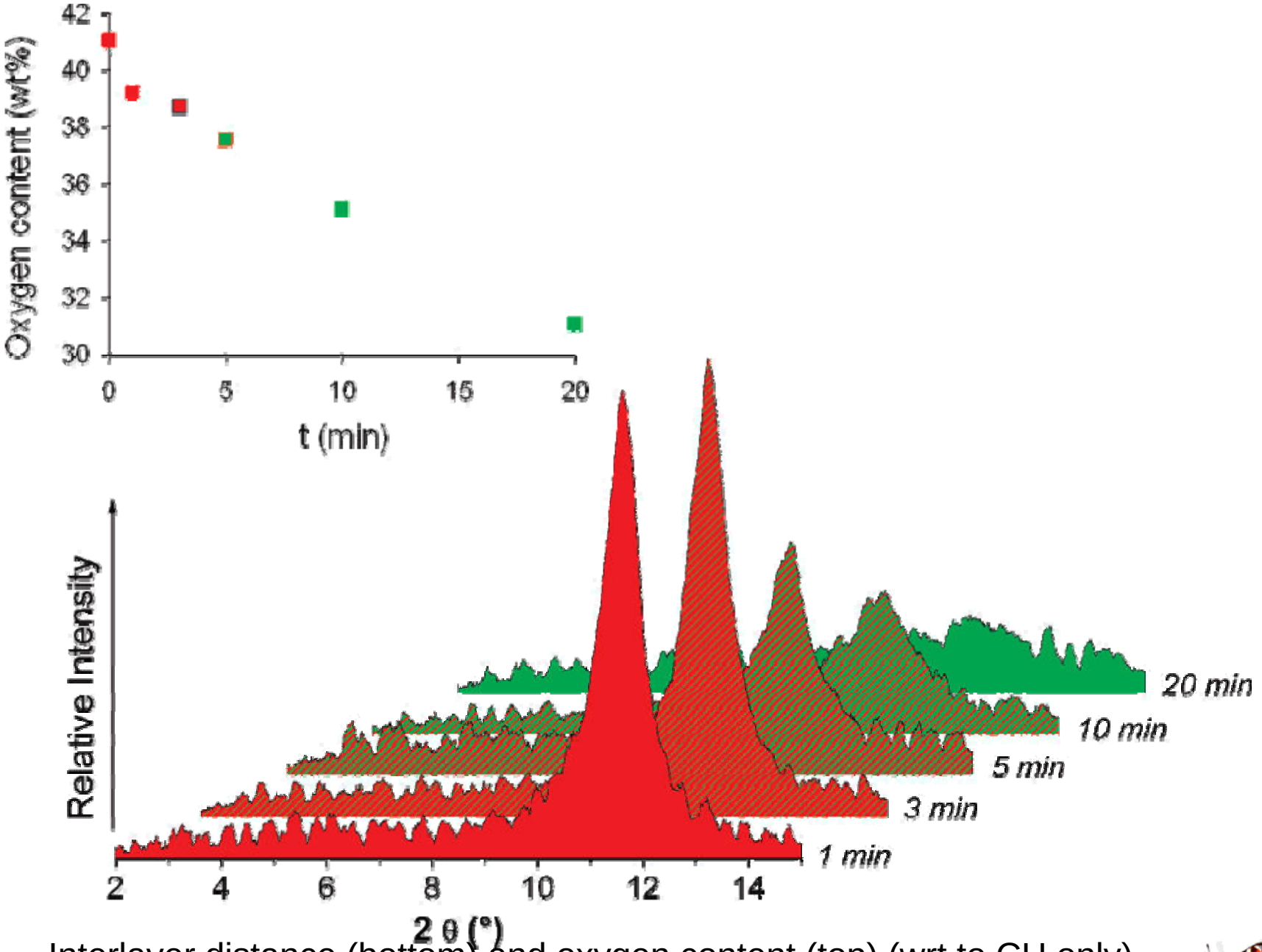
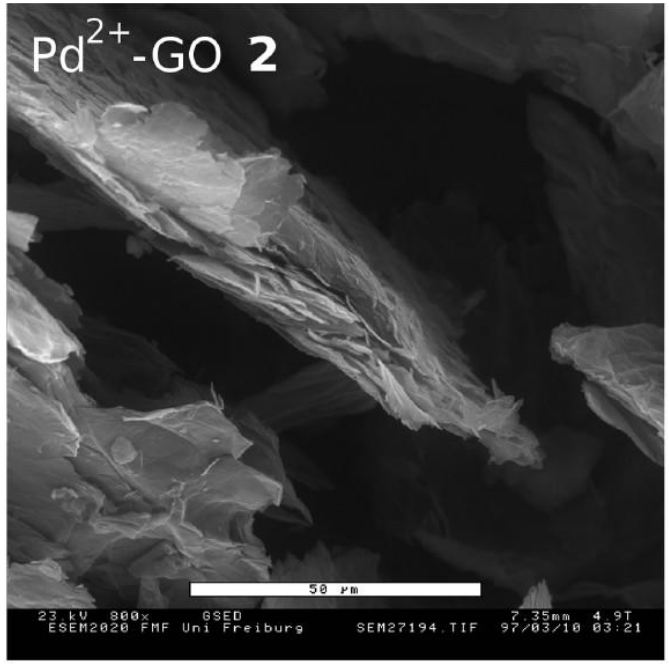
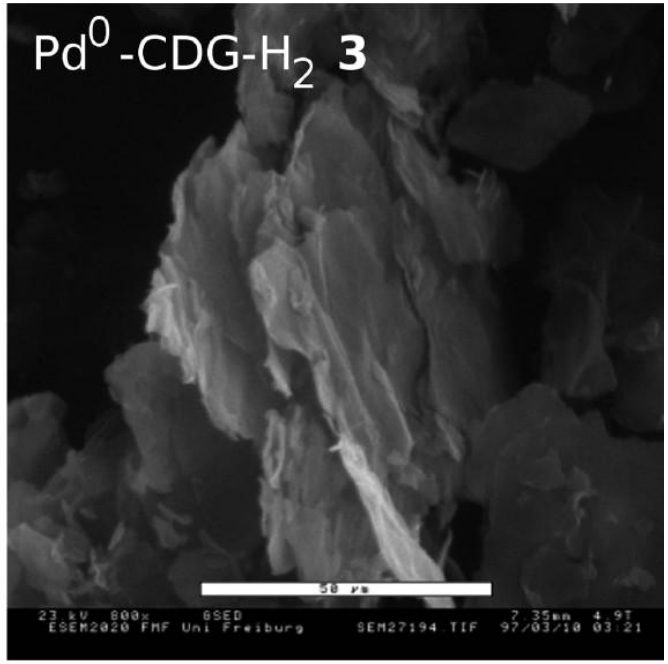


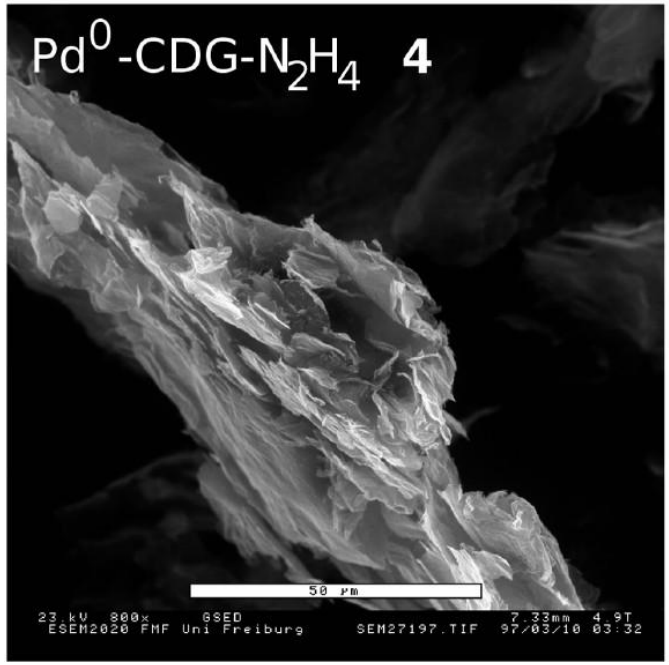
Figure 1. Thermogravimetric analysis of the catalysts under nitrogen.

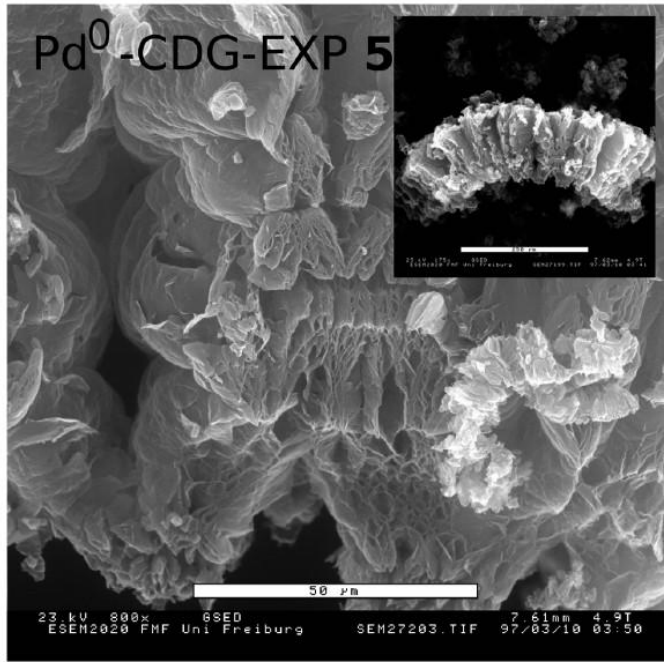


Interlayer distance (bottom) and oxygen content (top) (wrt to CH only) monitored by WAXS and elemental analysis, respectively, during reduction of Pd^{2+}-GO **2** with H_2.

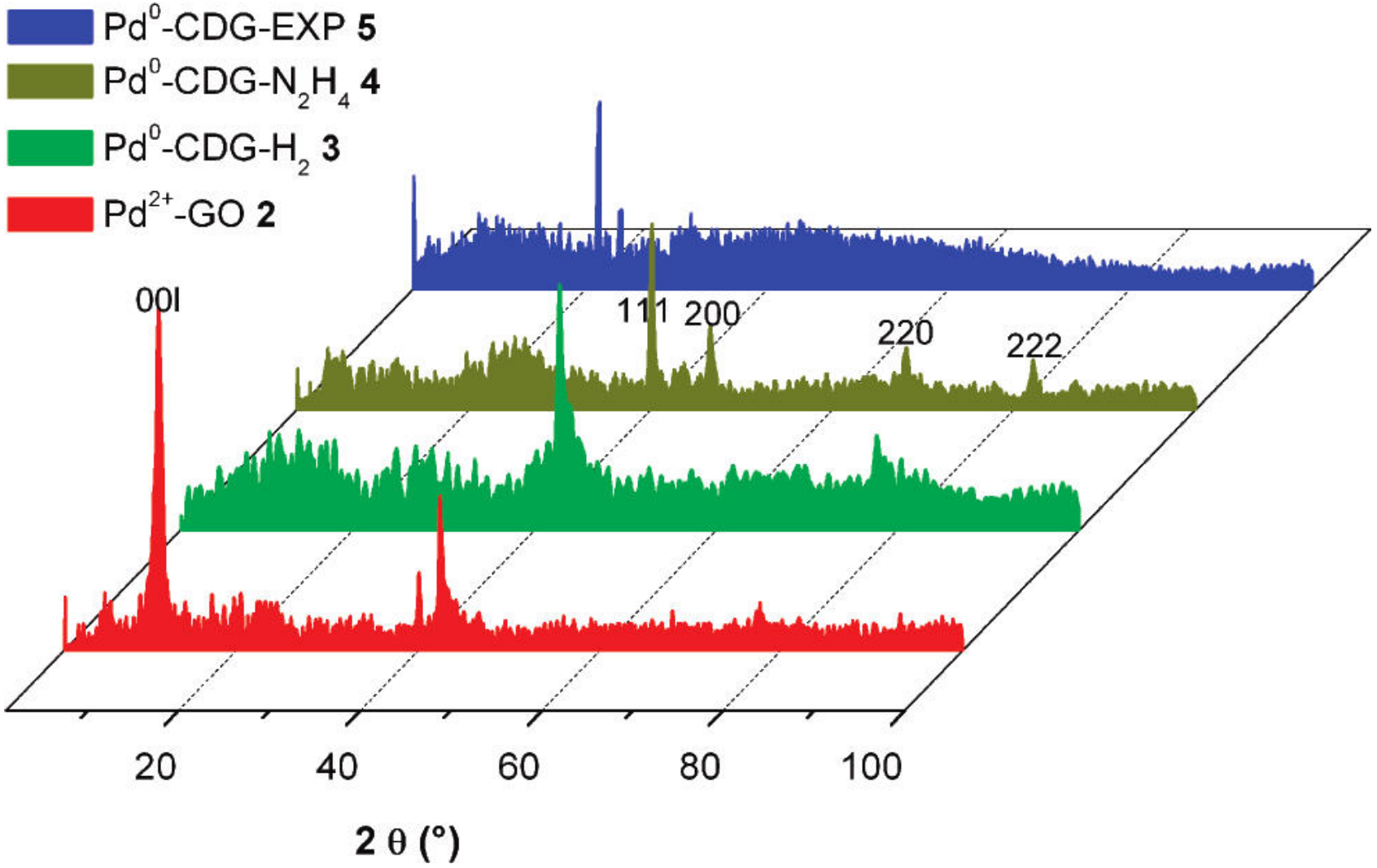








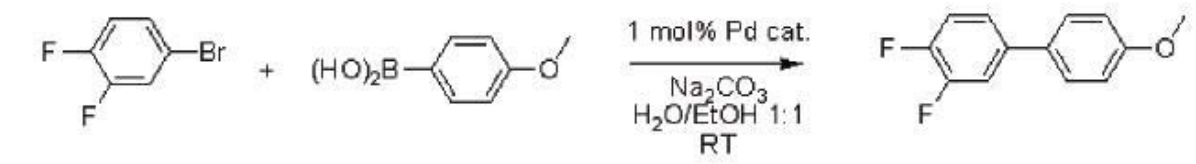
ESEM images of the catalysts

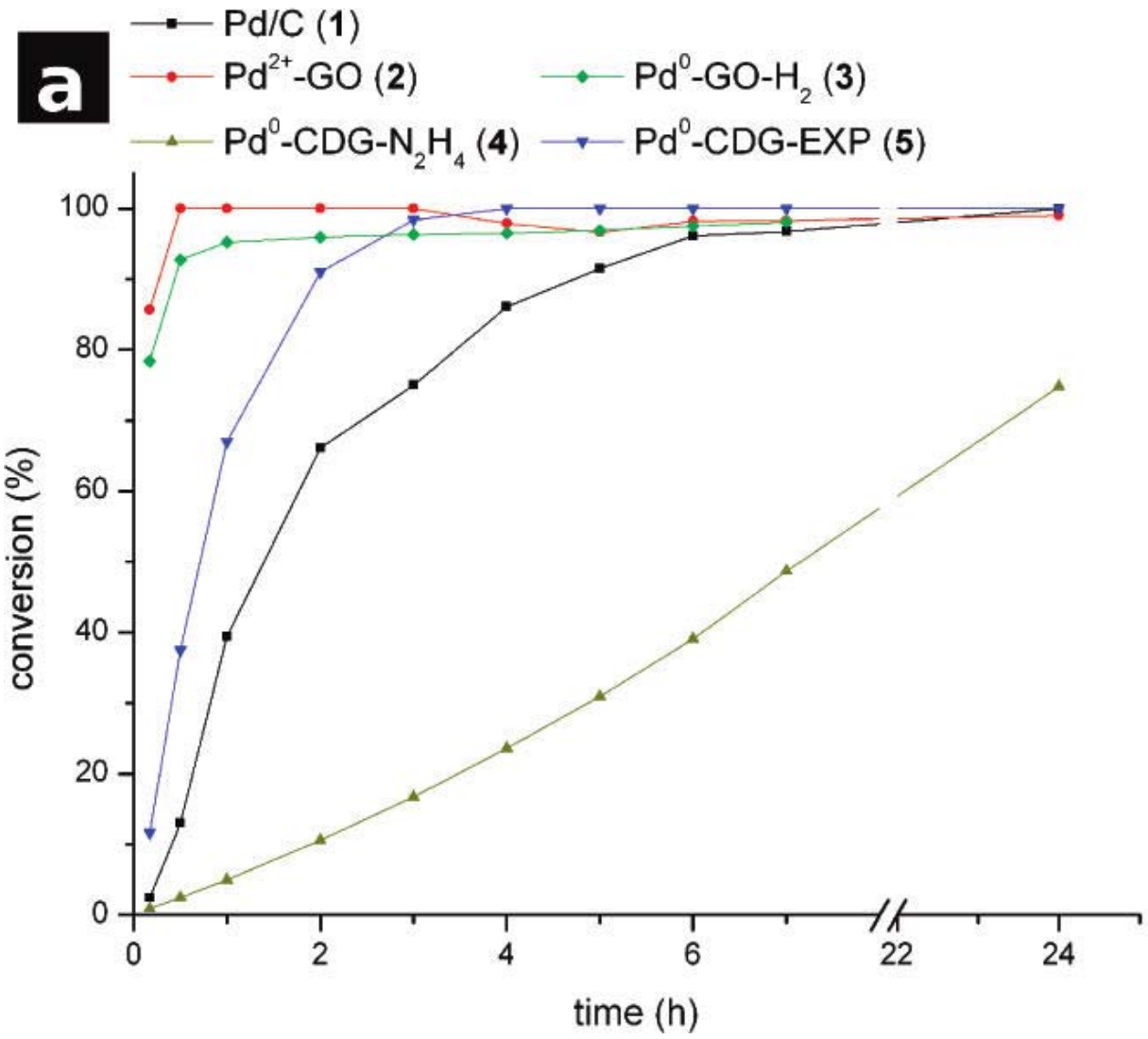


WAXS patterns of GO- and CDG-Pd composites.

Catalyst screening in the Suzuki-Miyaura reaction.

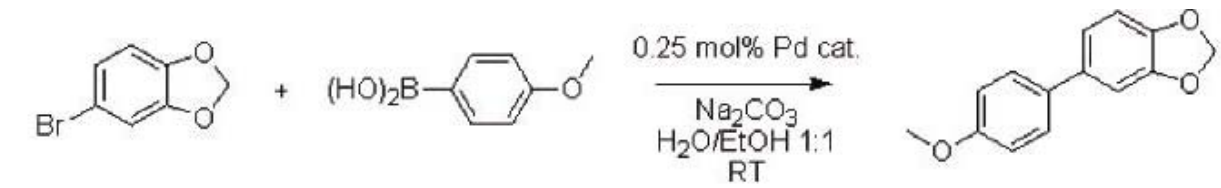
Comparison of Pd-GO/CDG catalysts 2-5 and Pd/C 1.

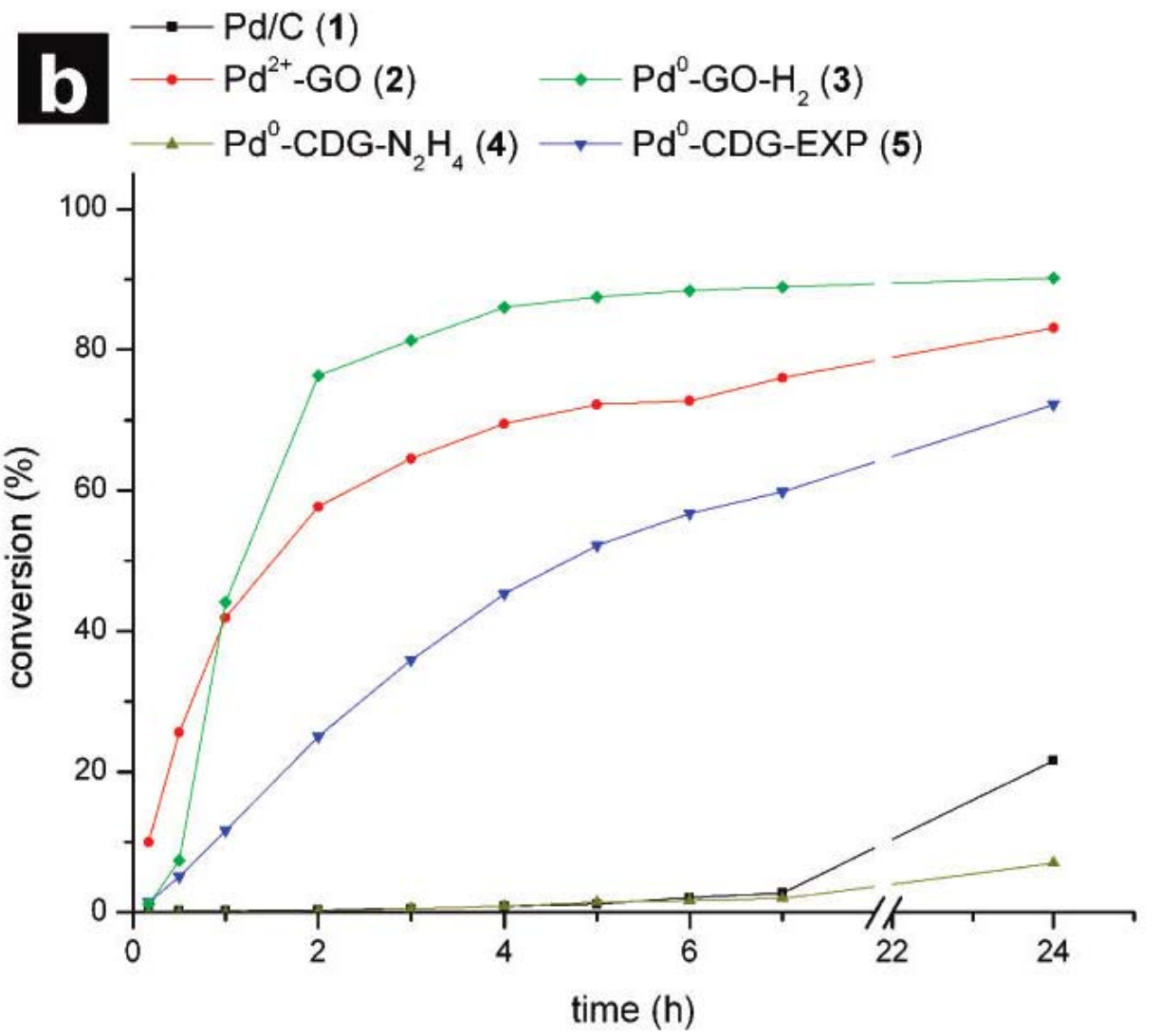




4-methoxyphenylboronic acid and 4-bromo-1,2-difluorobenzene

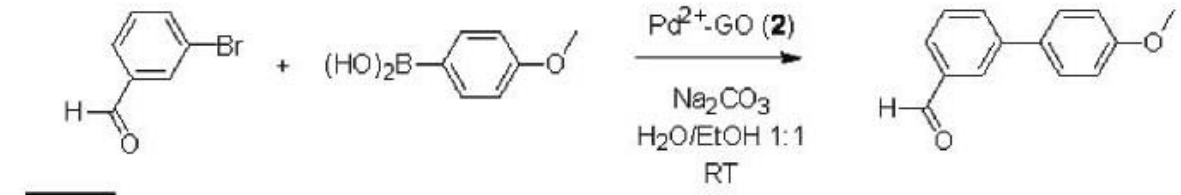
Catalyst screening in the Suzuki-Miyaura reaction. Comparison of Pd-GO/CDG catalysts 2-5 and Pd/C 1.

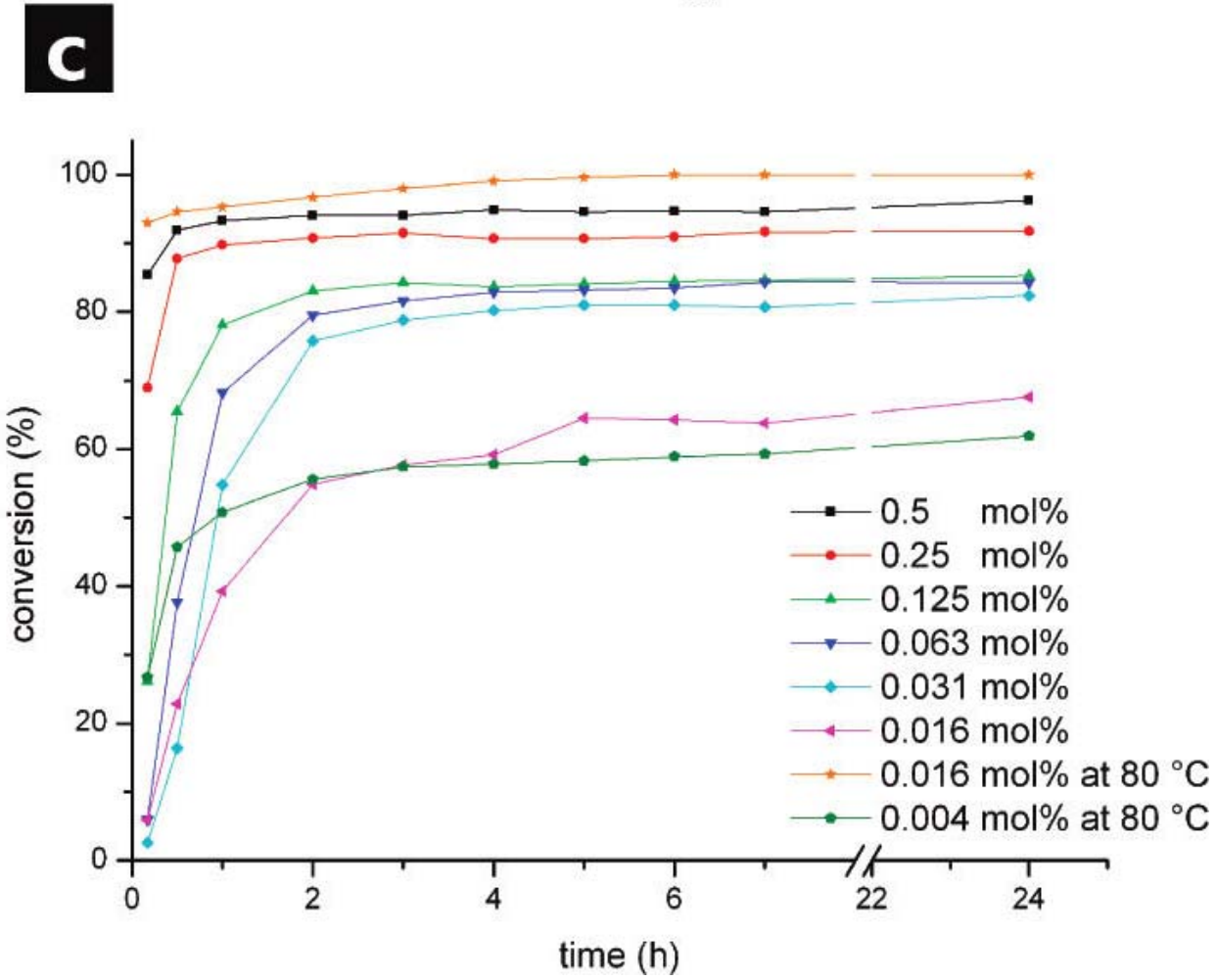




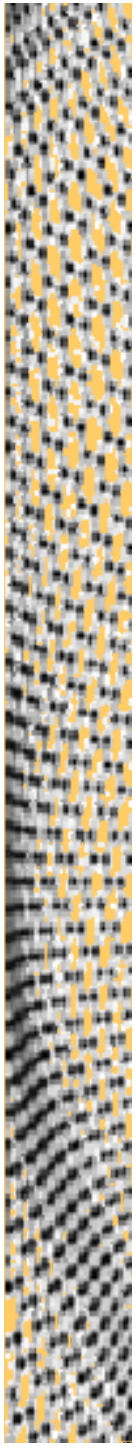
4-methoxyphenylboronic acid and 4-bromo-1,2-(methylene dioxy)benzene

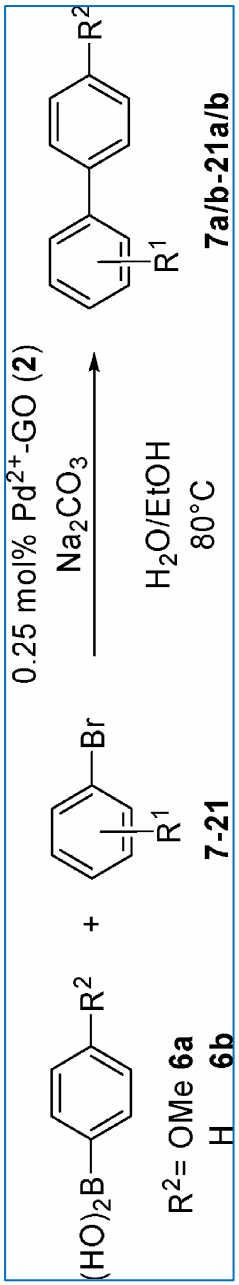
Catalyst screening in the Suzuki-Miyaura reaction. Comparison of Pd-GO/CDG catalysts 2-5 and Pd/C 1.





4-methoxyphenylboronic acid and 3-bromobenzaldehyde





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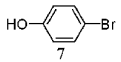
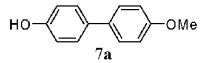
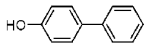
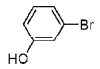
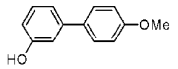
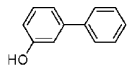
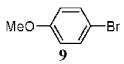
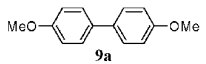
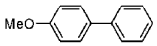
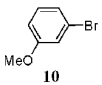
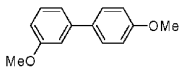
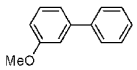
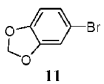
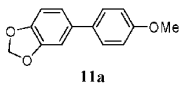
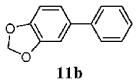
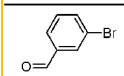
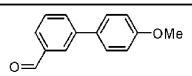
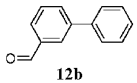
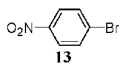
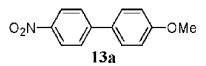
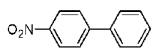
 7	-OMe	 7a	24 h	93%	84%
	-H	 7b	17 h	100%	96%
 8	-OMe	 8a	24 h	96%	86%
	-H	 8b	24h	94%	87%
 9	-OMe	 9a	4 h	100%	81%
	-H	 9b	4 h	100%	99%
 10	-OMe	 10a	4 h	100%	87%
	-H	 10b	4 h	96%	96%
 11	-OMe	 11a	8 h	97%	91%
	-H	 11b	8 h	98%	97%
 12	-OMe	 12a	4 h	100%	84%
	-H	 12b	4 h	100%	98%
 13	-OMe	 13a	4 h	100%	99%
	-H	 13b	4 h	100%	100%

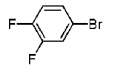
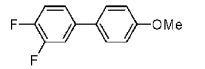
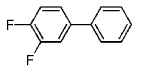
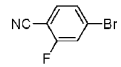
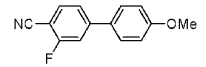
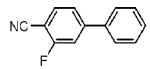
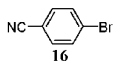
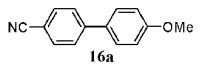
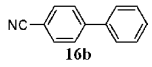
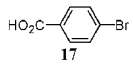
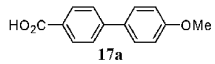
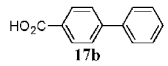
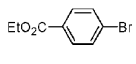
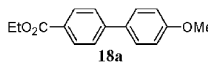
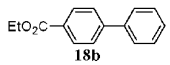
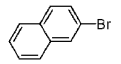
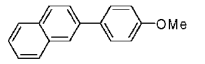
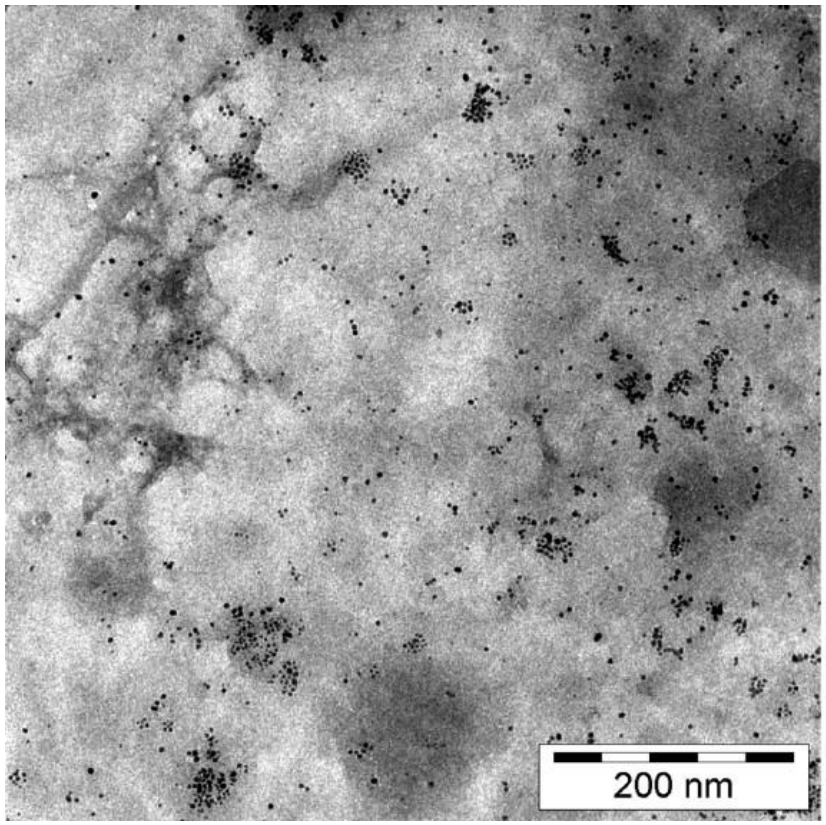
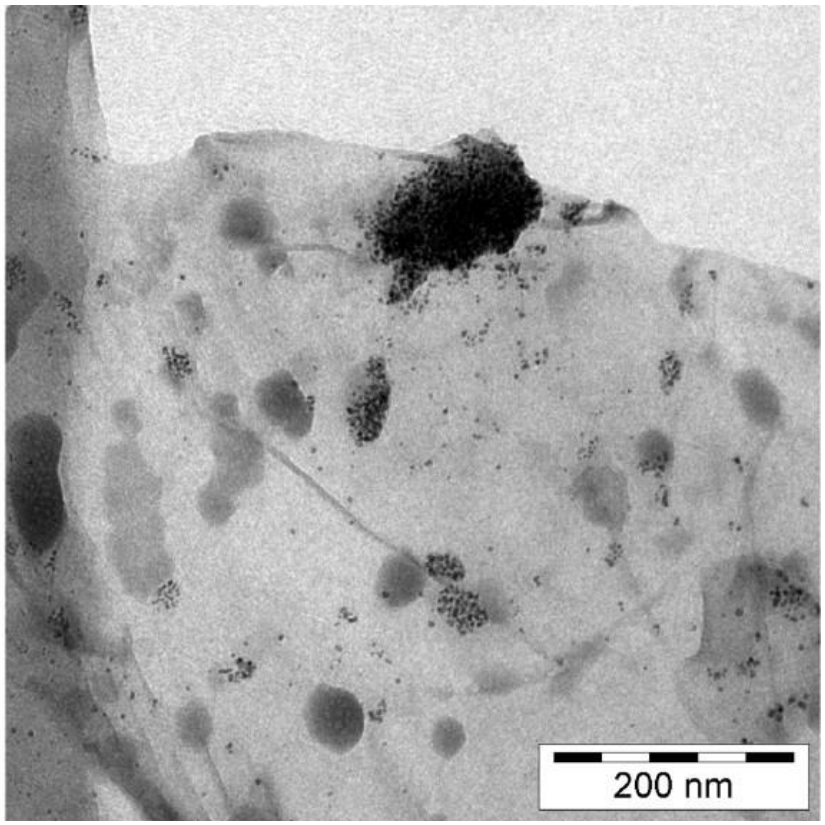
Arylbromide	R^2	Product	Time	Conversion	Yield
 14	-OMe	 14a	4 h	100%	100%
	-H	 14b	4 h	100%	97%
 15	-OMe	 15a	4 h	100%	94%
	-H	 15b	10 h	100%	92%
 16	-OMe	 16a	4 h	100%	89%
	-H	 16b	4 h	100%	96%
 17	-OMe	 17a	24 h	86%	83%
	-H	 17b	24 h	93%	94%
 18	-OMe	 18a	4 h	100%	93%
	-H	 18b	4 h	100%	87%
 19	-OMe	 19a	4 h	100%	96%
	-H	19b	4 h	100%	94%
20	-OMe	20a	24 h	36%	
	-H	20b	24 h	34%	
21	-H	21b	4 h	100%	100%

Table 3. Recycling Experiment with Pd^{2+}-GO **2**[a]

run	conversion (%)[b]
1	100
2	83
3	74
4	19





Pd particles formed on catalyst Pd^{2+}-GO **2** after the first run (left) and fourth run (right).

Conclusions

- Immobilization of Pd^{2+} on graphite oxide (GO) via cation exchange and subsequent chemical reduction to Pd^{0} nanoparticles and chemically derived graphenes (CDG).
- (GO)-Pd and the (CDG)-Pd catalysts were successfully applied to the Suzuki-Miyaura coupling reaction.
- Easy to handle as they are stable in air
- Extraordinary high activities with turnover frequencies (TOF) of up to 39000 h^{-1} and very low leaching make them an attractive alternative to commercially available Pd catalysts such as Pd on charcoal.
- Reuse of the catalysts can be achieved, with small loss in activity.
- Recovery of the noble metal is possible because of very low leaching.

Similar works with our system (Pt, Pd, Fe)

Thanks . . .