

Supplementary Materials

Tuning and enhancement of the Mizoroki-Heck reaction using polarized Pd nanocomposite carbon aerogels

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1. Reagents and solvents

All reagents were purchased from Sigma-Aldrich and were used without further purifications. Acetonitrile and CH₂Cl₂ were purchased from Scharlab and acetone from Panreac. They were used without further purifications.

2. Characterization techniques

Surface area determinations (S_{BET}) of Pd(0)-CAs were performed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using an ASAP-2000 surface area analyzer (Micromeritics Instruments Corp.). Samples of approximately 0.03 g were heated to 130 °C under vacuum (10^{-5} Torr) for at least 22 h to remove all absorbed species.

Bulk densities were estimated by measuring the dimensions and the mass of each monolithic sample.

Pd elemental analysis was performed by inductively coupled plasma optical emission (ICP-OES) using a Perkin-Elmer Optima 4300DV.

Powder X-ray diffraction (p-XRD) was obtained with a D5000 Siemens X-ray powder diffractometer using Cu_{K α} incident radiation.

Transmission electron microscopy (TEM) observations were performed using a JEOL JEM-2010 microscope operating at 200 kV.

Scanning electron microscope (SEM) were performed with the Quanta 200 ESEM FEG from FEI with a field emission gun (FEG) for optimal spatial resolution. The microscope was equipped with an **Energy Dispersive X-ray (EDX)** system chemical analysis.

Cyclic voltammetry and **chronoamperometry measurements** were made using a Princeton Applied Research VMP3 multichannel potentiostat controlled by the EC-Lab V9.54 software.

Gas Chromatography (GC) analysis was performed using an Agilent Technologies 7890A GC system equipped with an Agilent HP-5 column (30 m x 0.320 mm x 0.25 μm).

¹H and ¹³C NMR spectra were recorded with a Bruker AC250 NMR Spectrometer (250 MHz for ¹H and 62.5 MHz for ¹³C) with CDCl₃ as the solvent. ¹H shifts were referenced to CDCl₃ at 7.26 ppm. ¹³C shifts were referenced to CDCl₃ at 77 ppm.

Infrared spectroscopy measurements were carried out using the Total Attenuated Reflectance (ATR) technique, on a Perkin Elmer HART spectrophotometer, with a ZeSe flat plate accessory of 60 °.

3. Preparation of Pd(0)-CAs (electrode and catalyst)

A suspension of 2,4-dihydroxybenzoic acid (2.9 g 18.8 mmol) in distilled water (100 mL) was treated with K₂CO₃ (1.3 g, 9.4 mmol) under vigorous stirring, in the presence of air. The suspension became clear after 0.5h, when all the acid was neutralized. Formaldehyde (3.0 g, 37 wt%, 37 mmol) was then added to the solution, followed by the catalyst K₂CO₃ (26 mg 0.19 mmol). The clear solution was poured into glass moulds that were then sealed hermetically. In one of the moulds were introduced the graphite rods (see the *current collectors* section). The mixture was allowed to cure for 24 h at room temperature, and 96 h at 70 °C. Next, the gels and the graphite rods were poured to a water solution and each gel was punctured with a graphite rod. The gels with the graphite rod were first washed with acetone and then soaked in a 0.1 M solution of Pd(OAc)₂ in acetone for 24 h; this procedure was repeated three times. Then the gels were washed with acetone and dried with supercritical CO₂ inside the autoclave (procedure: (1) exchange of acetone by liquid CO₂, at rt and 100 bar, over 2 h and (2) drying with supercritical CO₂ at 45 °C, 120 bar, over 2 h), obtaining the Pd(0) organic aerogels electrocatalysts. Finally, the material was pyrolyzed at 1050 °C under N₂ in a tubular furnace to afford the Pd(0)-CAs electrocatalysts.

4. Preparation of Pd(0)-CAs

Pd(0)-CAs catalysts were synthesized in the same way that Pd(0)-CAs described above without introducing the graphite rod in the gel structure.

5. Current collectors

Two types of graphite rods were used as current collectors: a) commercial pencil leads (CPLs) from Staedtler, B, $\phi = 0.9$ mm, composition: 71% graphite, 23% clay, 5% wax and 1% impurities; and b) pure graphite rods (PGRs) from Carbon Lorraine, Ellor + 30, $\phi = 1$ mm, composition: 99.9% graphite and 0.1% impurities. Prior to synthesis, the

graphite rods were filed, treated with 1M aqueous solution of KOH during 24 h, washed with water until neutralization and finally dried by evaporation. A metal wire was not use as current collector in order to avoid any possible interference in catalysis.

6. Cyclic Voltammetry measurements (Figures S1-S4)

Unless otherwise specified, all the cyclic voltammetry measurements were performed in one-compartment cell with a Teflon cap provided with several holes for electrodes. A three-electrode system composed of a working electrode (indicated in each measurement), a platinum cylinder (9 cm²) as counter electrode and a platinum wire (0.6 mm of diameter) as quasireference electrode were used. All the measurements were performed using 75 ml of 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) in acetonitrile as electrolyte.

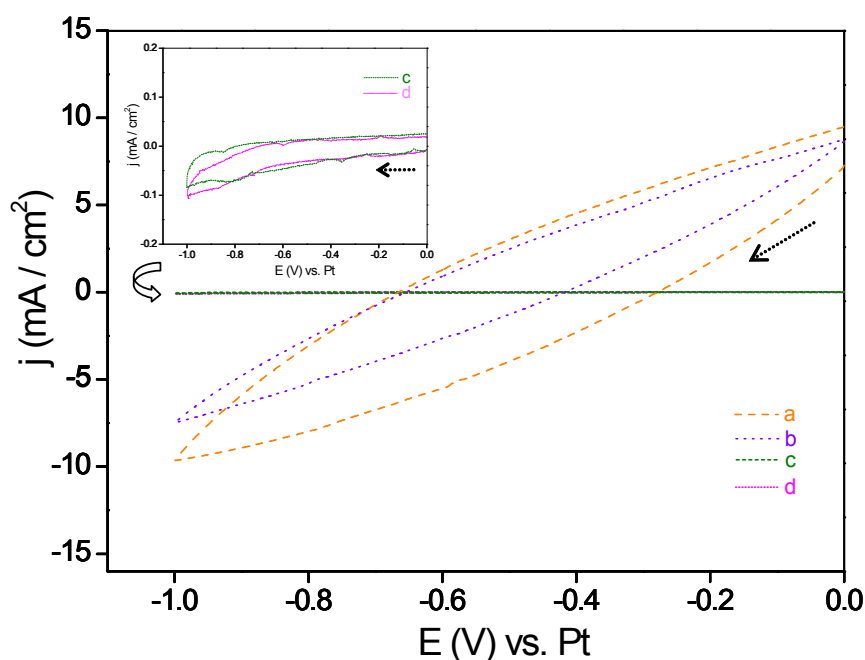


Fig. S1- Comparison of current densities values vs. potential, of different working electrodes (Pd(0)-CAs) and current collectors: a, Pd(0)-CA with pure graphite rod (orange); b, Pd(0)-CA with commercial pencil lead (violet); c, pure graphite rod (PGR) (green) and d, commercial pencil lead (CPL) (pink). The scan rate was 20 mV s⁻¹ in all measurements. According to the results of current density, we can observe a high difference between Pd(0)-CAs and current collectors. The results showed that Pd(0)-CA with PGR (orange) presented the highest current density values, with small differences when compared with Pd(0)-CA with CPL (violet).

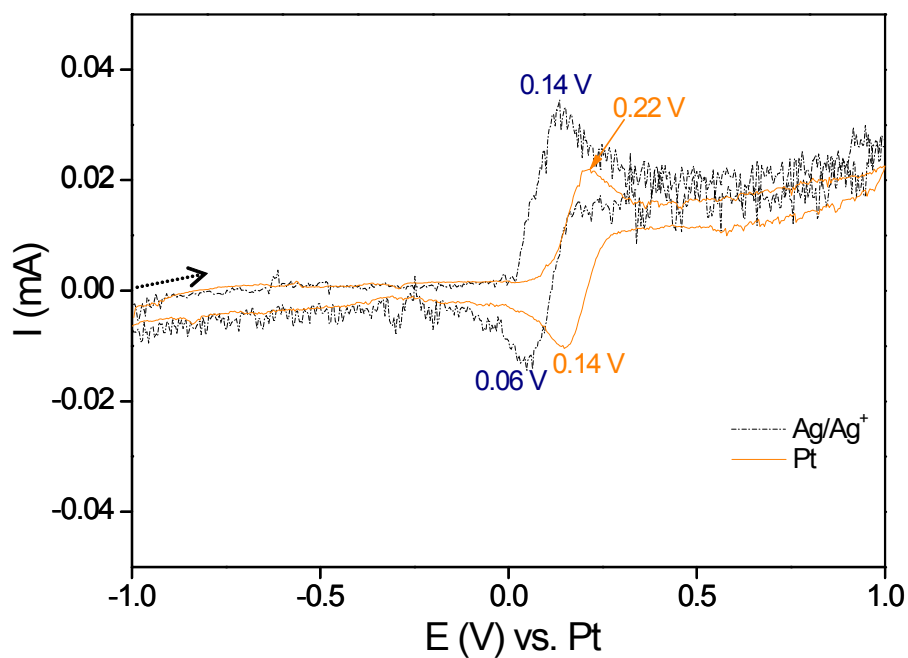


Fig. S2- Comparison of Ag/Ag⁺ reference electrode vs. Pt quasireference electrode, using ferrocene as standard. The Ag/Ag⁺ reference electrode was purchased from BAS Inc. (ref.: 012172 RE-7S, non aqueous reference electrode). It was composed by a Ag wire using 0.01 M AgNO₃ and 0.1 M tetrabutylammonium perchlorate in CH₃CN as electrolyte. The Pt quasireference electrode was a Pt wire. In both measurements the working electrode was a CPL and the scan rate was 10 mV s⁻¹. Ferrocene (15 mg) was used as standard and added to the electrolyte solution in each measurement. The potential measured *versus* to the Pt quasireference electrode and to a Ag/Ag⁺ reference electrode only differs in 0.08 V.

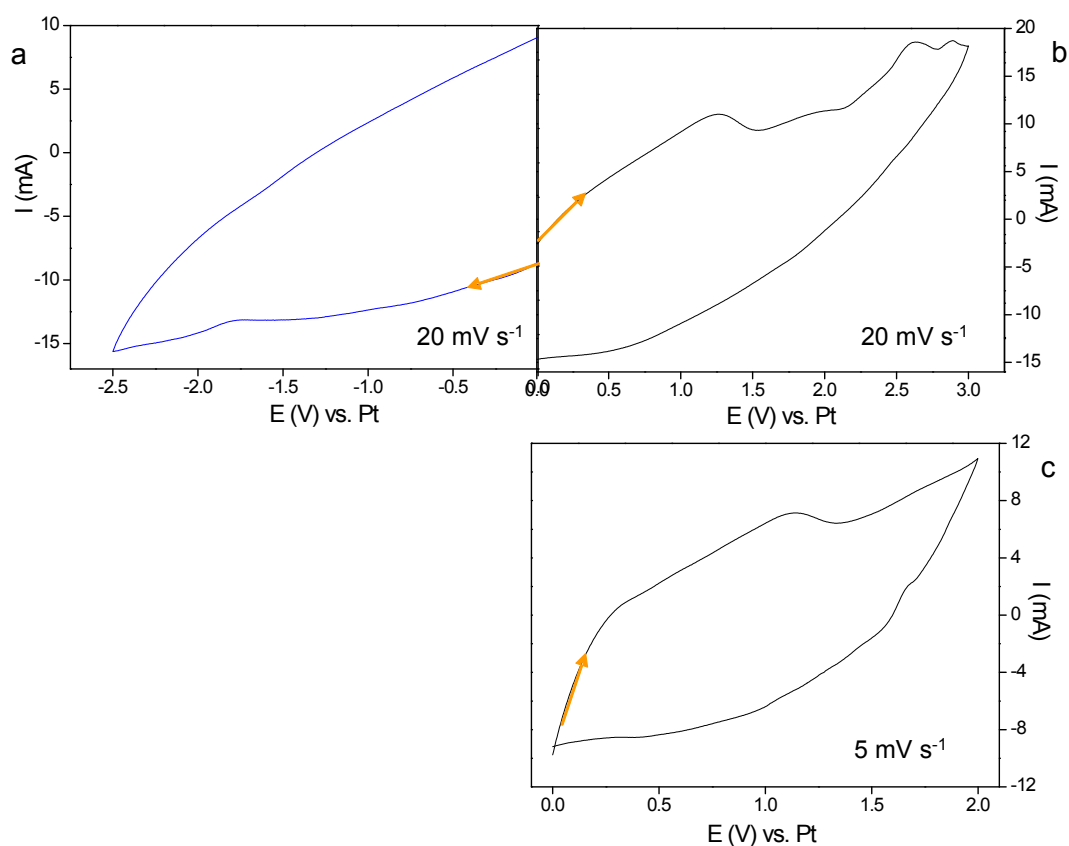


Fig. S3- Cyclic voltammograms of Pd(0)-CA as working electrode using CPL as current collector. **a**, Reduction potentials (scan rate of 20 mV s^{-1}): we can observe that a reduction starts at -1.8 V . **b**, Oxidation potentials (scan rate of 20 mV s^{-1}): a current decrease and then several peaks are showed from $+1.2 \text{ V}$, corresponding to several oxidations. **c**, To be sure that any oxidation occurred in the potential range from 0 to $+1 \text{ V vs. Pt}$, we decided to carry out a cyclic voltammetry using a lower scan rate (5 mV s^{-1}). In the voltammogram, we can observed that the current decrease also takes place from $+1.2 \text{ V}$, the same as was observed in case b. This results confirm that neither reductions nor oxidations of Pd(0) occurred in the potencial range of electrocatalytic reactions (from $+1$ to -1 V vs. Pt).

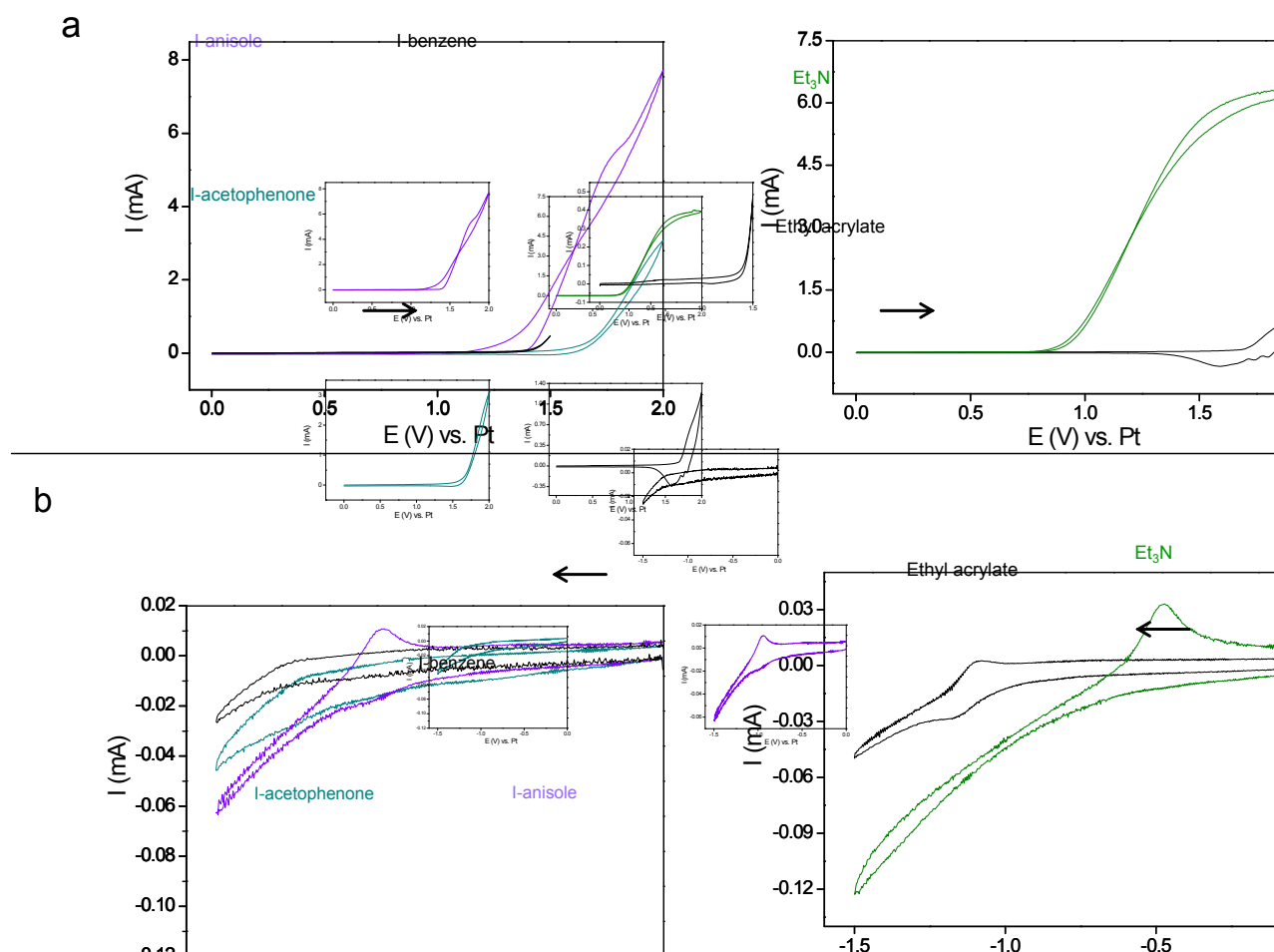


Fig. S4- Cyclic voltammetry measurements of substrates used in the Heck reaction.

a, Oxidation potentials and b, reduction potentials. The working electrode was a CPL and the scan rate was 20 mV s^{-1} , in all measurements. The quantities of substrates added to the electrolyte solution were: 0.7 ml (6 mmol) of iodobenzene (**I-benzene**), 1.40 g (6 mmol) of 4-iodoanisole (**I-anisole**), 0.49 g (2 mmol) of 4-iodoacetophenone (**I-acetophenone**), 2 ml (12 mmol) of ethyl acrylate and 1.7 ml (18 mmol) of Et_3N . Lower quantity of 4-iodoacetophenone was used due to its low solubility in CH_3CN at rt. According to the voltammograms, none of the compounds showed peaks in the potential range used in the electrocatalytic Heck reaction (from -1 to +1 V vs. Pt), except Et_3N and 4-iodoanisole. In the case of Et_3N , the oxidation starts at +0.85 V and the reduction is sharply observed from -0.6 V. Nevertheless, this redox activity of Et_3N observed from -1 to +1 V vs. Pt, did not appear to influence the electrocatalytic Heck reactions results (*see below*), probably because Et_3N was used in excess (2 equivalents of Et_3N with respect to the limiting reagent). On the other hand, when reduction potentials are applied the voltammogram of 4-iodoanisole presented a reduction process which is

clearly observed from -0.95 V. This process can not interfere in the reaction because in the case of 4-iodoanisole we use a potential between 0.0 V and + 0.5 V.

7. General procedure for Pd(0)-CA catalyzed M-H reactions

Ethyl acrylate (2 ml, 18 mmol), aryl iodide (6 mmol) and triethylamine (1.7 ml, 12 mmol) were dissolved in 25 mL of acetonitrile using a 100 ml three necked round-bottom flask. Then, Pd(0)-CA was added to the mixture and the reaction was carried out under reflux (90 °C), in the presence of air and mechanical stirring. Periodic sampling of the reaction media was made to analyze the reaction evolution by GC and ¹H-NMR measurements. When the reaction was over, the solution was decanted and the Pd(0)-CA washed several times with acetonitrile. The combined solvent extracts were evaporated, the residue was dissolved in CH₂Cl₂ and the solution was washed with aqueous NaHCO₃ and a saturated solution of NaCl. The organic extract was evaporated to afford the coupling product (see the *Analytical data of the coupling products* in page 16)

The Pd(0)-CA was always submerged in CH₃CN 24 h before its use and kept in the same solvent.

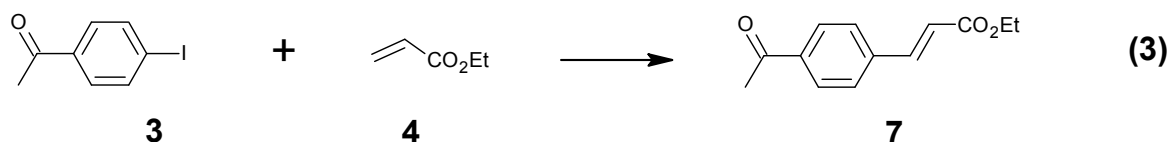
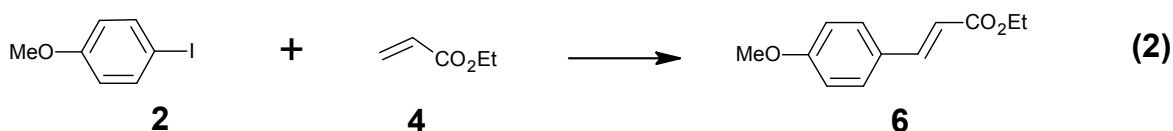
8. General procedure for Pd(0)-CA catalyzed M-H reaction under electric stimulus

One-compartment cell formed by a round-bottom glass piece and a Teflon cap was used. The Teflon cap was provided with several holes for electrodes, refrigerant and to add or remove solution. A three-electrode system composed of Pd(0)-CA as working electrode, a platinum cylinder (9 cm²) as counter electrode and a platinum wire (0.6 mm of diameter) as quasireference electrode were used. The reactions were carried out under reflux (90 °C), in the presence of air, magnetic stirring and constant potential, monitoring current versus time. Ethyl acrylate (18 mmol), aryl iodide (6 mmol) and triethylamine (12 mmol) were dissolved in 25 mL of acetonitrile. In some cases a solution of 25 ml of 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) in acetonitrile as electrolyte was used. Periodic sampling of the reaction media was made to analyze the reaction evolution by GC and ¹H-NMR measurements. When the reaction was over, the solution was decanted and the Pd(0)-CA washed several times with acetonitrile. The combined solvent extracts were evaporated, the residue was dissolved in CH₂Cl₂ and the solution was washed with aqueous NaHCO₃ and a saturated solution

of NaCl. The organic extract was evaporated to afford the coupling product (see the *Analytical data of the coupling products* in page 16).

The Pd(0)-CA was always submerged in CH₃CN 24 h before its use and kept in the same solvent.

9. Chronoamperometry measurements of M-H reactions with different aryl iodides (Figure S5).



The reactions were carried out at 90 °C in CH₃CN (25 ml) with magnetic stirring, aryl iodide (4-iodoanisole (2) or 4-iodoacetophenone (3)) (6 mmol), ethyl acrylate (4) (18 mmol) and triethylamine (12 mmol) as a base, to obtain ethyl *trans*-4-methoxycinnamate (6) or ethyl *trans*-4-acetylcinnamate (7) as final products respectively. The working electrode was a Pd(0)-CA with CPL as current collector.

The **Figure S5** shows, that the + 0.5 V (vs. Pt) reactions, with both aryl iodides, presented the same behaviour of current vs. time described in the main article. At the beginning of the reaction, there were very low current values, and they increased up to a maximum, in parallel when the reaction started to occur. Then, the current started to decrease until its stabilization, which, in these cases, it indicated that the reaction was ending. So, here, the current also appears as an indirect measure of the reaction evolution. In the case of I-anisole, the 3 h time period presented the behaviour described before and the 5.5 h time period showed the stabilization of the current since the reaction was ending. The fact that the current values of 5.5 h period were higher than the values of 3 h period, probably were due to a high polarization of the electrode.

In the 0.0 V (vs. Pt) reactions, the current values obtained during the course of the reaction were between ±0.2 mA, and they could be positive or negative, since reduction or oxidation potentials were not applied. The I-acetophenone measurements of 0.0 V showed the same behaviour described for +0.5 V, but presenting low current values.

The I-anisole 0.0 V measurements presented a maximum of negative values, being different as obtained with I-acetophenone. Then, the current started to decrease where its stabilization was not very clear. The variations of current values observed after the maximum, could be produced partially by the polarization of the electrode and the background of the potentiostat. With 0.0 V reactions, not always is possible to use the current as an indirect measure of the reaction evolution since the current values are too low to get a clear relationship between them.

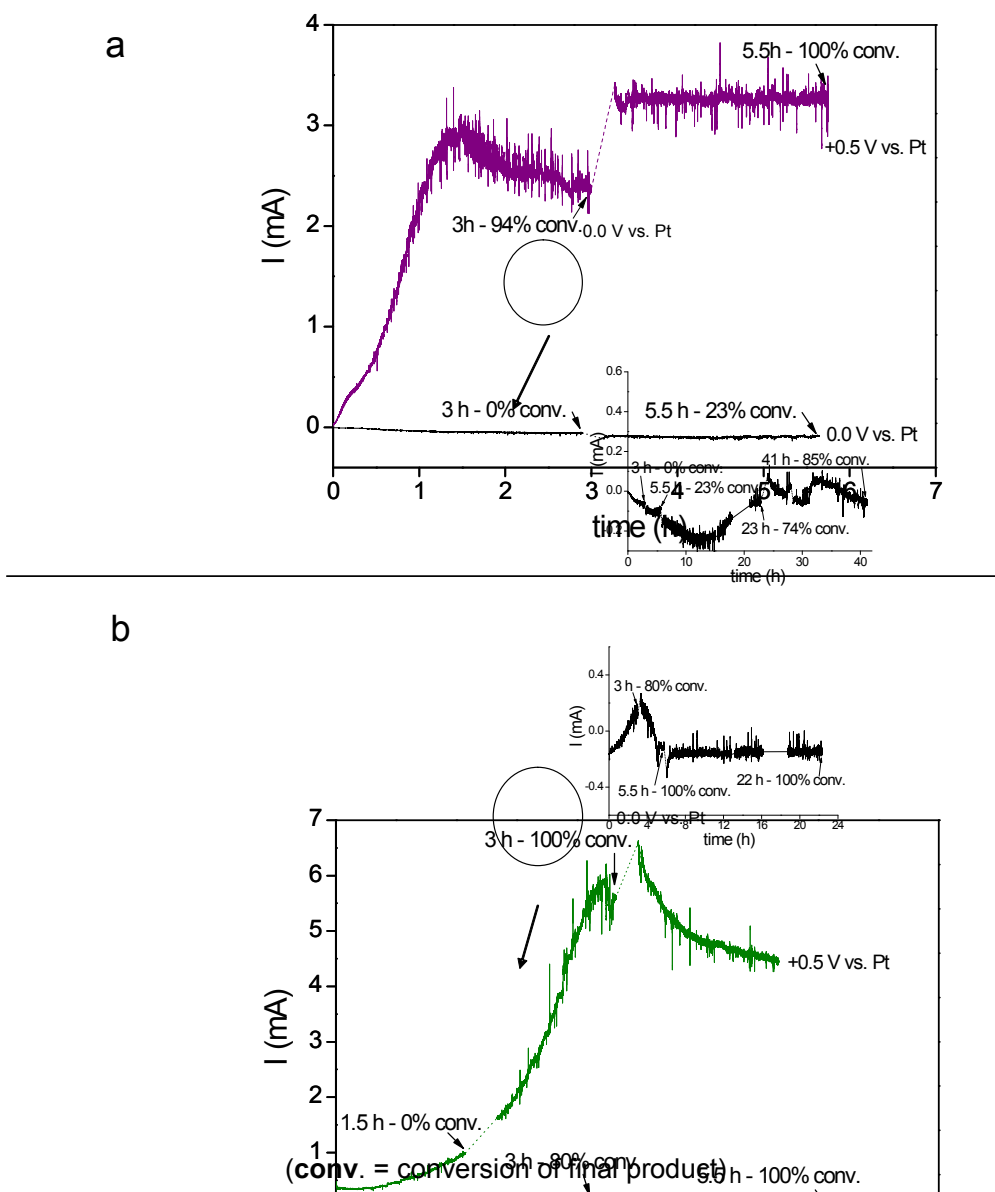


Fig. S5- Chronoamperometry measurements of M-H reactions with a, 4-iodoanisole and b, 4-iodoacetophenone, (reactions 2 and 3 respectively). Comparison of +0.5 V with 0.0 V reactions. Time reaction and conversion results are also described in Table 2, entries 9-12 (main article). The gap after each time control (represented by dots) corresponds to the time sampling.

10. SEM and EDX results of Pd deposited on Pt(C) and electrocatalytic cell (Figures S6-S8)

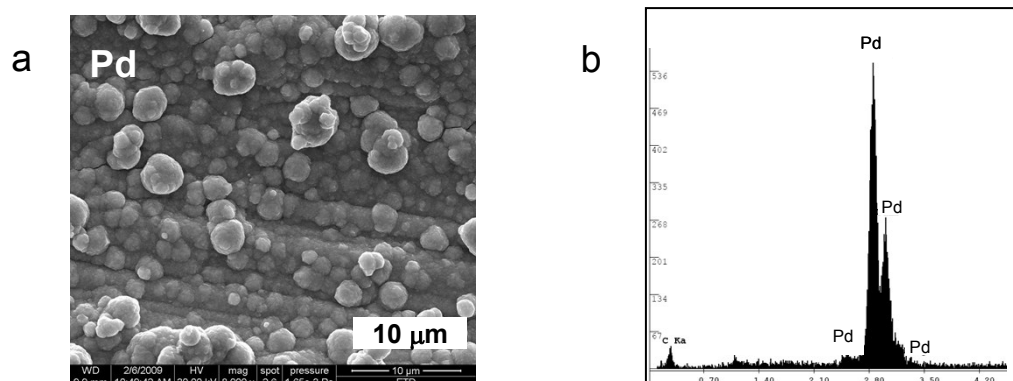


Fig. S6- Pd deposited on Pt(C) at the end of $E > 0$ Heck reaction. a, SEM image and b, the corresponding EDX results, which confirm the presence of Pd.

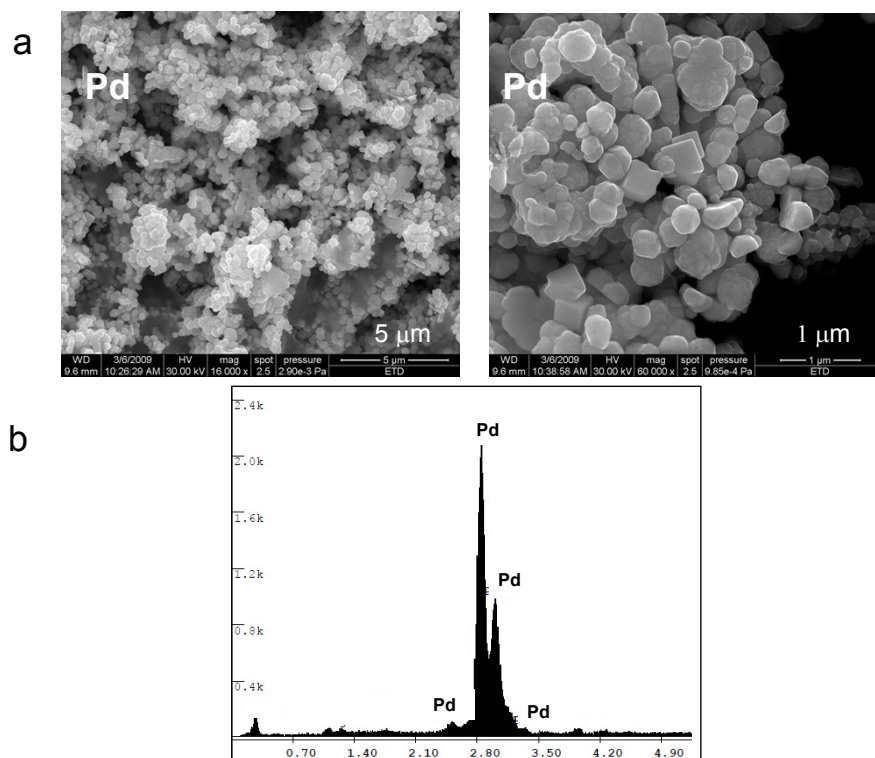


Fig. S7- Pd deposited on the electrocatalytic cell at the end of $E > 0$ Heck reaction. a, SEM images and b, the corresponding EDX results, which confirm the presence of Pd.

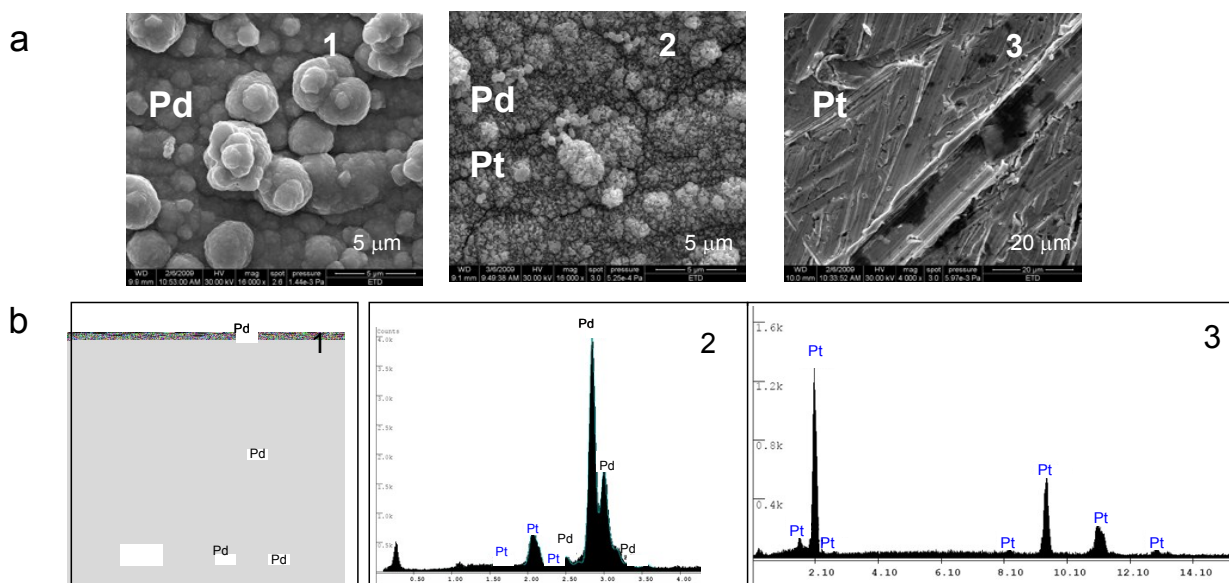


Fig. S8- Pd deposition and removal from Pt(C). **a**, SEM images and **b**, the corresponding EDX results. These results (SEM and EDX) corresponds to a negative potential reaction carried out subsequently to a positive potential reaction without doing the Pd recovery process (section 5), so it means that the $E < 0$ reaction started with Pd deposited on Pt(C):

1, Pt(C) just before the $E < 0$ reaction started: there is Pd deposited on Pt(C) and Pt is not detected by EDX.

2, Pt(C) after the $E < 0$ was applied in a period of time during the course of the Heck reaction. The SEM image shows more wrinkled particles than figure 1 and the EDX detected Pd and Pt. According to these results and the experimental observations, we can say that Pd was being excavated from the Pt(C) while the $E < 0$ was applied, during the course of the Heck reaction.

3, Pt(C) at the end of the Heck reaction ($E < 0$). Pd deposition was not observed on Pt(C) and only Pt was detected (SEM image and EDX results). These results confirm that all Pd has been removed from Pt(C).

11. Complementary M-H essays under electric field (Tables S1-S4)

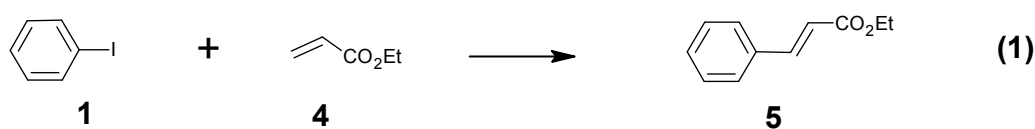


Table S1- Comparison of results using or not an electrolyte solution

Entry	Potential E (V)	Time (hours)	Yield (%)
			ethyl <i>trans</i> -cinnamate (%)
1 (with electrolyte)	+0.5	3	99
2 (without electrolyte)	+0.5	3/4/5.5	94/99/99
3 (with electrolyte)	-1	4/20	66/74
4 (without electrolyte)	-1	4/21	48/62
5 (with electrolyte)	+1	3/5.5	92/96
6 (without electrolyte)	+1	3/5.5	89/94

Pd(0)-CA with 7 mol% of Pd was used as catalyst and electrode. TBABF₄ (0.1 M) was employed as electrolyte.

Table S2- Results of Pd(0)-CA recyclability. Two different methods to recover the Pd deposited back to the Pd(0)-CA.

Entry ^b	Pd(0)-CA (cycle number)	Potential E (V)	Time (hours)	Yield (%)
				ethyl <i>trans</i> -cinnamate
1 ^a	1 st cycle	+0.5	3	99
2 ^a	2 nd cycle	-0.5	3	98
3 ^a	3 rd cycle	+0.5	3	98
4 ^a	4 th cycle	-1	3	98
5 ^a	5 th cycle	+1	3/5.5	92/96
6 ^a	6 th cycle	+0.5	3/5.5/22	77/89/89
7	7 th cycle	+0.5	3/5.5/22	73/86/86
8	8 th cycle	-0.5	3/5.5/22	12/51/57
9	9 th cycle	-1	3/5.5/22	23/55/69

The same Pd(0)-CA (7 mol% of Pd) was used nine consecutive times. ^aTBABF₄ (0.1 M) was employed as electrolyte. ^bEntries 1-4: For reactions using positive potential and when conversion was close to 100%, deposition of black palladium on the Pt counter electrode Pt(C) and throughout the cell was observed, as mentioned in the text. The Pd was recovered during the consecutive E < 0 reaction (E = -0.5 or -1V) (see also Table S3 below); Entries 5-7: In this cases the process of Pd recovery was performed adding 30 ml of the electrolyte solution (0,1 M TBABF₄ in CH₃CN) and applying -1 V vs. Pt at 90 °C under magnetic stirring before the next reaction; Entries 8 and 9: Pd deposition was not observed at E < 0.

Table S3- Comparison of positive ($E > 0$) and negative ($E < 0$) potential reactions when the $E < 0$ was performed consecutively to the $E > 0$ ($E < 0$ started with Pd deposited on the Pt(C) (anode)). Experiments using electrolyte and without using were tested.

Entry	Pd(0)-CA (cycle number)	Potential E (V)	Time (hours)	Yield (%) ethyl <i>trans</i> -cinnamate
1 ^a	1 st cycle	+0.5	3	98
2 ^a	2 nd cycle	-0.5	3	99
3 ^a	3 rd cycle	+0.5	3	97
4 ^a	4 th cycle	-1	3	98
5	1 st cycle	+0.5	3/4/5.5	94/99/99
6	2 nd cycle	-1	3/4	99/99

Pd(0)-CAs with 7 mol% of Pd was used as catalyst and electrode. ^aTBABF₄ (0.1 M) was employed as electrolyte. For reactions using positive potential and when conversion was close to 100%, deposition of black palladium on the Pt counter electrode Pt(C) and throughout the cell was observed as mentioned in the text. The Pd was recovered during the consecutive $E < 0$ reaction ($E = -0.5$ or $-1V$).

Table S4- M-H essays with alternating current (A.C.). Electrolyte was not used.

Entry	Potential E (V)	Time (hours)	Yield (%) ethyl <i>trans</i> -cinnamate
1	+0.5 (60 s) / -0.5 (60 s)	3	99
2	+0.5 (15 s) / -0.5 (15 s)	3/5.5/21	73/89/90
3	+0.5 (30 s) / -0.5 (30 s)	3/5.5/21	64/76/91
4	+0.5 (60 s) / -0.5 (120 s)	3/5.5	35/72
5	+0.5 (5 s) / -0.5 (10 s)	3/5.5	19/45

Pd(0)-CA with 5 mol% of Pd was used as catalyst and electrode.

The aim of this process was to find out the optimal point between having: 1) high rate (achieved with positive potentials) and 2) no palladium deposition (achieved with negative potentials, because they promote the return of palladium to CA).

12. TEM and powder XRD results of Pd(0)-CA after 9 cycles (Figures S9-S10)

Pd(0)-CA after 9 cycles of M-H reactions under an electric external field (Table S2) (Figures S9-S10)

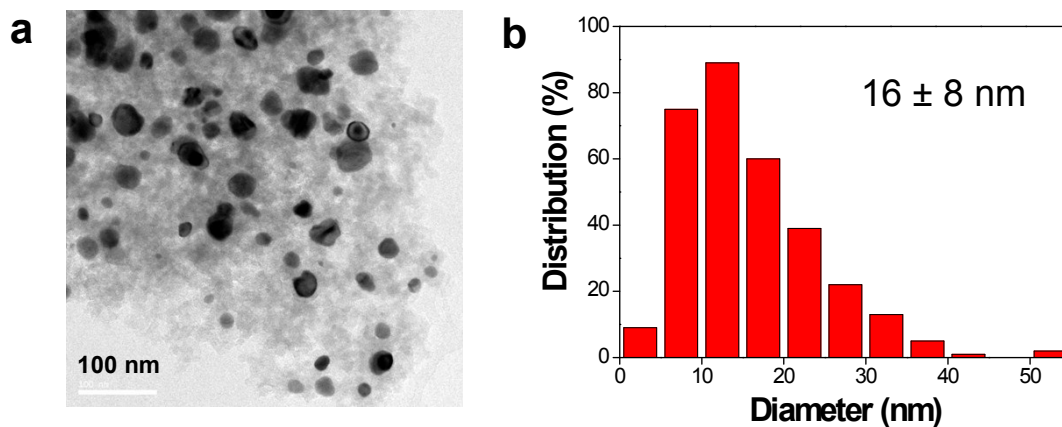


Fig. S9- TEM results. **a**, TEM image; **b**, particle size distribution. The mean particle diameter (16 ± 8 nm) was determined by TEM.

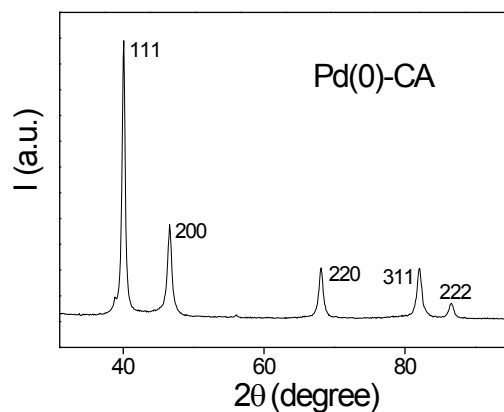


Fig. S10- Powder XRD results

13. Rationalization of the current intensity evolution during the electrically activation of the M-H reaction (fig. S11).

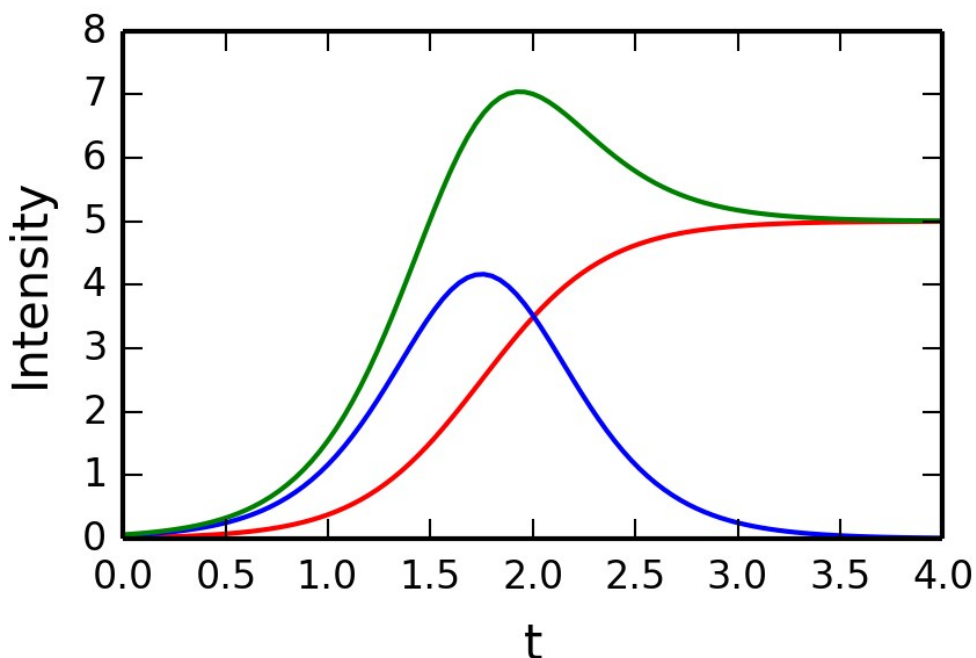
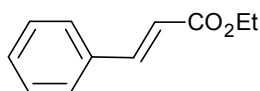


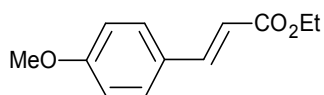
Fig. S11. The observed intensity profiles (shaped as the green line, i.e. see Fig.3A) appear as being a contribution of two kinds of cations (Fig.4): those of reaction intermediates (like $[\text{XPd}(\text{CH}_3\text{CN})_2(\text{Et}_3\text{N})]^+$, $\text{X}=\text{H},\text{Ar}$; blue line) and reaction products (like $(\text{Et}_3\text{N})^+$, red line). As intensity depends, except of geometrical parameters, on charge, ion mobility and species concentration, intensity profiles are directly related with the reaction mechanism and kinetics.

14. Analytical data of the Mizoroki-Heck reactions coupling products



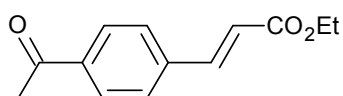
Ethyl *trans*-cinnamate, 5: oil (1.01 g; 95%); ^1H NMR (250 MHz, CDCl_3): δ 7.69 (d, $J = 16$ Hz, 1H), 7.56-7.49 (m, 2H), 7.41-7.35 (m, 3H), 6.44 (d, $J = 16$ Hz, 1H), 4.27 (q, $J = 7.17$ Hz, 2H), 1.34 (t, $J = 7.13$ Hz, 3H); ^{13}C NMR (62.5 MHz, CDCl_3): δ 167.0, 144.6, 134.5, 129.9, 128.9, 127.8, 118.3, 60.5, 14.4; IR (ATR): 2982, 1708, 1637, 1309, 1164, 1036, 978, 766, 684 cm^{-1} .

Ref. S. Martínez, A. Vallribera, C. L. Cotet, M. Popovici, L. Martín, A. Roig, M. Moreno-Mañas and E. Molins, *New J. Chem.*, 2005, **29**, 1342



Ethyl *trans*-4-methoxycinnamate, 6: oil (1.22 g; 98%); $^1\text{H NMR}$ (250 MHz, CDCl_3): δ 7.64 (d, $J = 16$ Hz, 1H), 7.47 (d, $J = 8.75$ Hz, 2H), 6.90 (d, 8.75 Hz, 2H), 6.30 (d, $J = 15.75$, 1H), 4.25 (q, $J = 7.17$ Hz, 2H), 3.83 (s, 3H), 1.33 (t, $J = 7.13$ Hz, 3H); $^{13}\text{C NMR}$ (62.5 MHz, CDCl_3): δ 167.4, 161.5, 144.4, 129.8, 127.3, 115.9, 114.4, 60.4, 55.5, 14.5; IR (ATR): 2979, 2840, 1705, 1634, 1603, 1511, 1248, 1158, 1028, 982, 827 cm^{-1} .

Ref. S. Mun, J.-E. Lee and J. Yun *Org. Lett.* 2006, **8**, 4887.



Ethyl *trans*-4-acetylcinnamate, 7: oil (1.26 g; 96%); $^1\text{H NMR}$ (250 MHz, CDCl_3): δ 7.97 (d, $J = 8.50$ Hz, 2H), 7.69 (d, $J = 16$ Hz, 1H), 7.60 (d, $J = 8.25$ Hz, 2H), 6.52 (d, $J = 16$ Hz, 1H), 4.28 (q, $J = 7.17$ Hz, 2H), 2.61 (s, 3H), 1.34 (t, $J = 7.13$ Hz, 3H); $^{13}\text{C NMR}$ (62.5 MHz, CDCl_3): δ 197.3, 166.5, 143.1, 138.9, 138.0, 128.9, 128.2, 120.9, 60.8, 26.7, 14.4; IR (ATR): 2978, 1712, 1683, 1637, 1604, 1311, 1262, 1173, 1034, 981, 827, 680 cm^{-1} .

Ref. Y. Chen, L. Huang, M. A. Ranade and P. X. Zhang, *J. Org. Chem.* 2003, **68**, 3714.