Electronic Supplementary Material (ESI) for RSC Advances.

Microwaves-promoted solventless Heck−Mizoroki reactions catalyzed by Pd nanoparticles supported on laponite clay

Alejandro V. Martínez, Fabio Invernizzi, Alejandro Leal, José A. Mayoral, José I. García*

Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Departamento de Química Orgánica, CSIC-Universidad de Zaragoza, calle Pedro Cerbuna, 12, E-50009 Zaragoza, Spain
Phone: +34 976762271, e-mail: ji.garcia@csic.es

Content

1. Gas chromatography analyses of the Heck coupling reactions

1.1 Heck coupling reaction of iodobenzene with n-butyl acrylate

FID from Agilent 6890-II, Agilent J&W GC Columns HP-5: 30 m ×0.25 mm × 0.25 µm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20°C min^{-1} to 250 °C (7.5 min); retention times: n-butyl acrylate: 2.6 min, n-decane: 3.4 min, iodobenzene: 3.7 min, (*E*)-butyl cinnamate: 8.7 min.

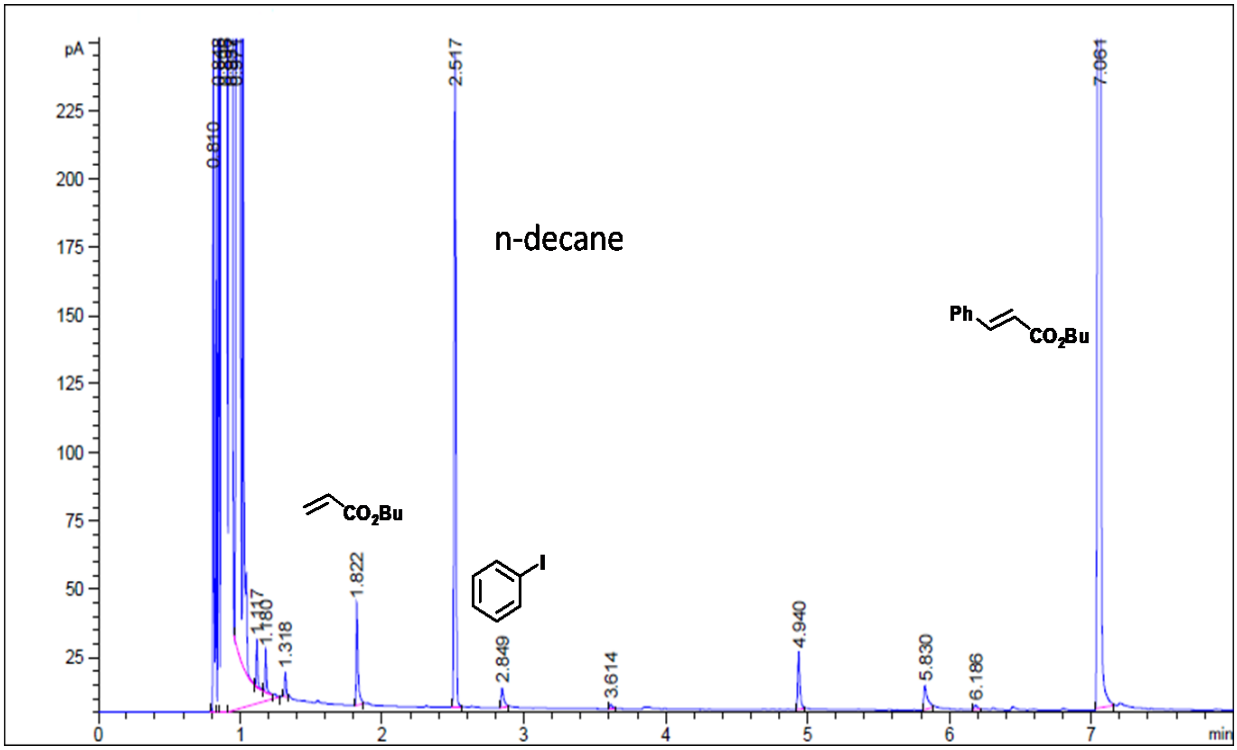

Fig. S1. Typical CG chromatogram for the Heck coupling reaction of iodobenzene with n-butyl acrylate.

In order to determine the Heck coupling yield n-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$Yield(\%) = 1.163 \cdot \frac{decane\ mmol \cdot cinnamate\ area}{iodobenzene\ mmol \cdot decane\ area} \cdot 100$$

$$Conversion(\%) = \left(1 - 0.617 \cdot \frac{decane\ mmol \cdot iodobenzene\ area}{iodobenzene\ mmol \cdot decane\ area}\right) \cdot 100$$

2. NMR analysis of (*E*)-butyl cinnamate

2.1 ^{1}H-NMR.

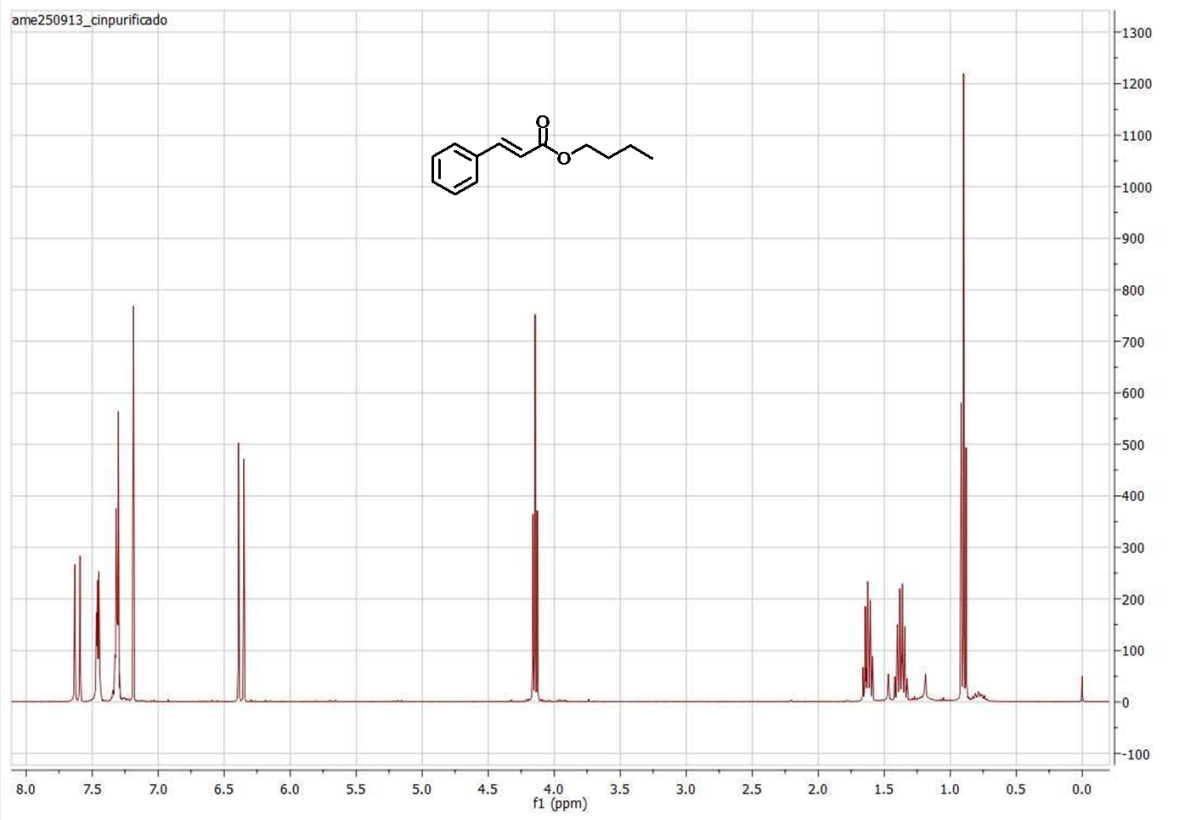

Fig. S2. ^{1}H-NMR spectrum of n-butyl cinnamate.

2.2 ^{13}C-NMR (APT).

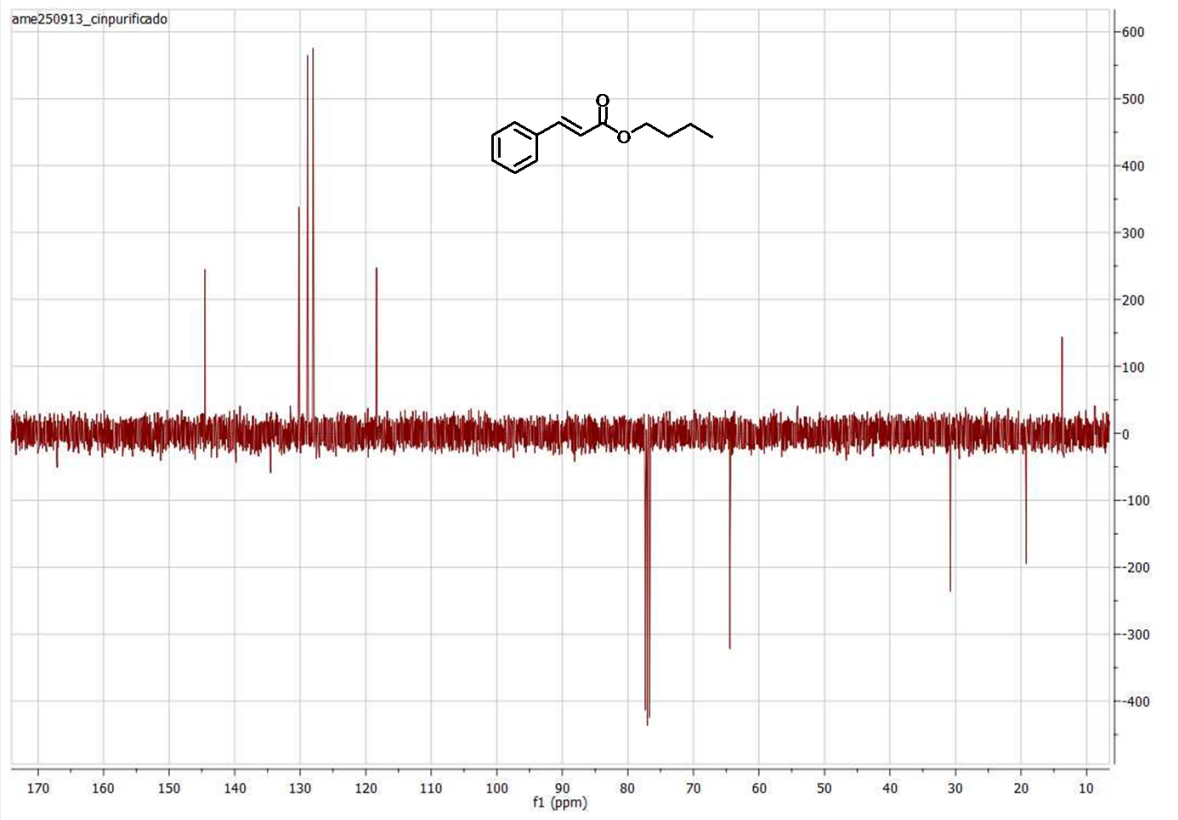

Fig. S3. ^{13}C-RMN (APT) spectrum of n-butyl cinnamate.

2.3 HSQC [^{1}H-^{13}C(APT)-NMR].

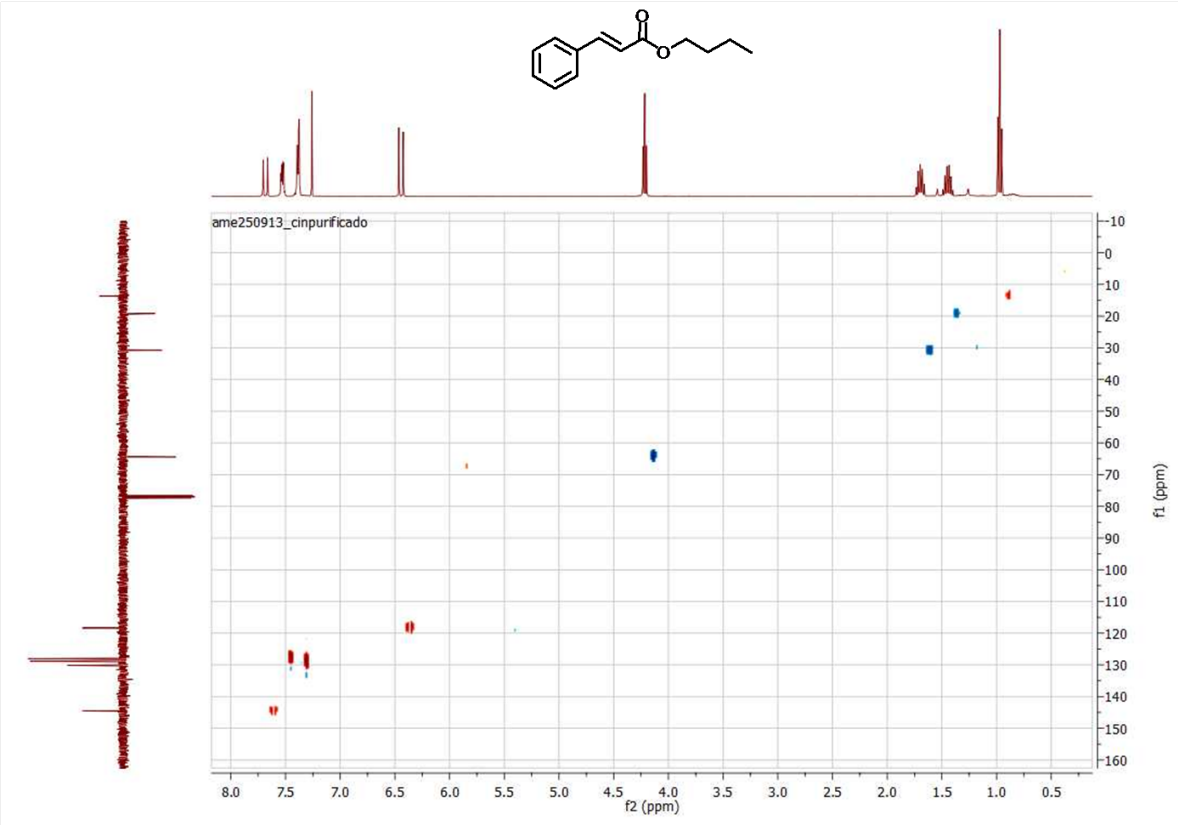

Fig. S4. HSQC [^{1}H-^{13}C(APT)] NMR spectrum of n-butyl cinnamate.

3. Thermogravimetric analyses of freshly prepared and exhausted catalytic systems

3.1 Laponite

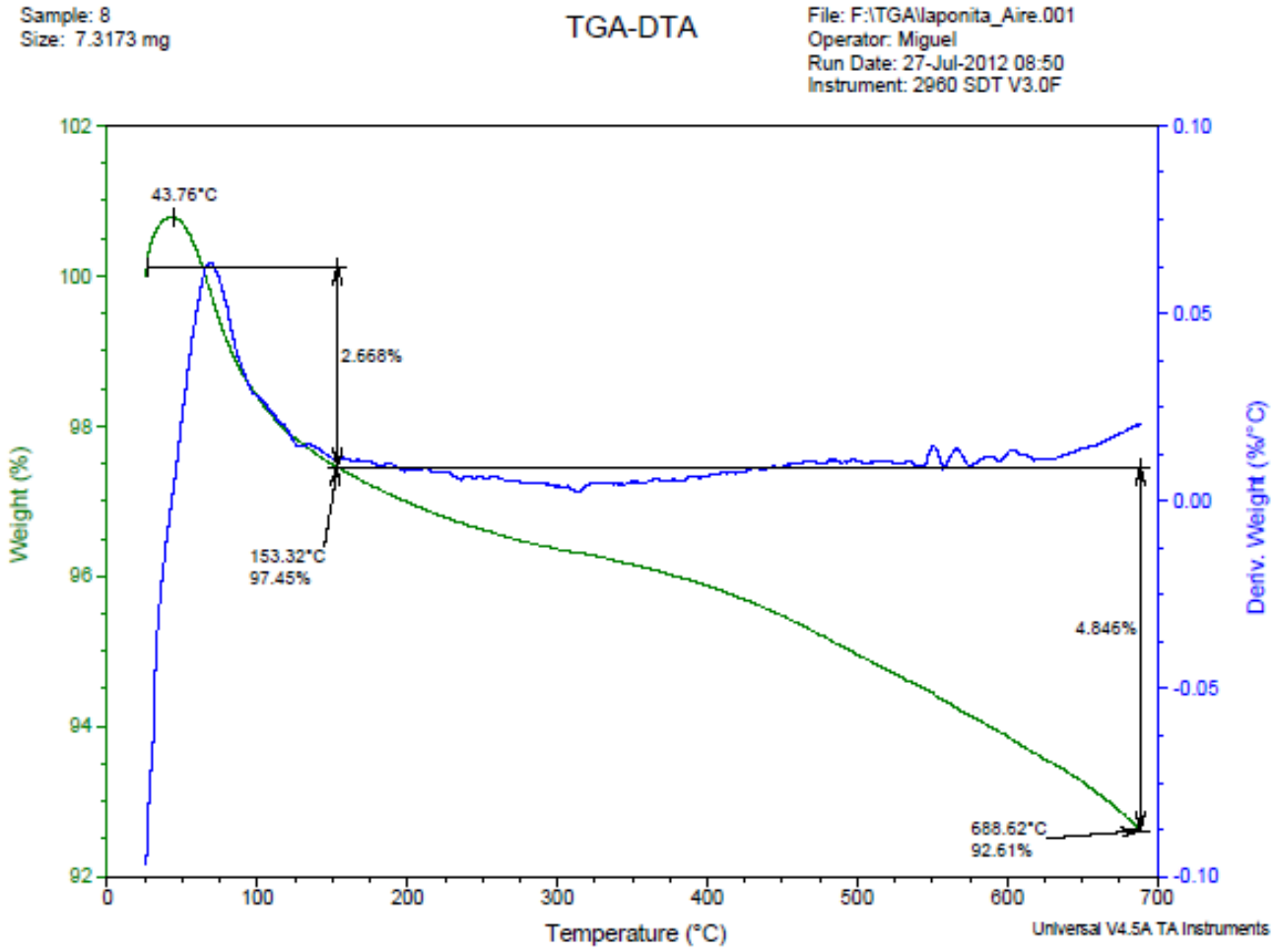

Fig. S5. TGA of laponite

3.2 Freshly prepared Pd-PVP@[bmim][PF_6]-laponite catalyst

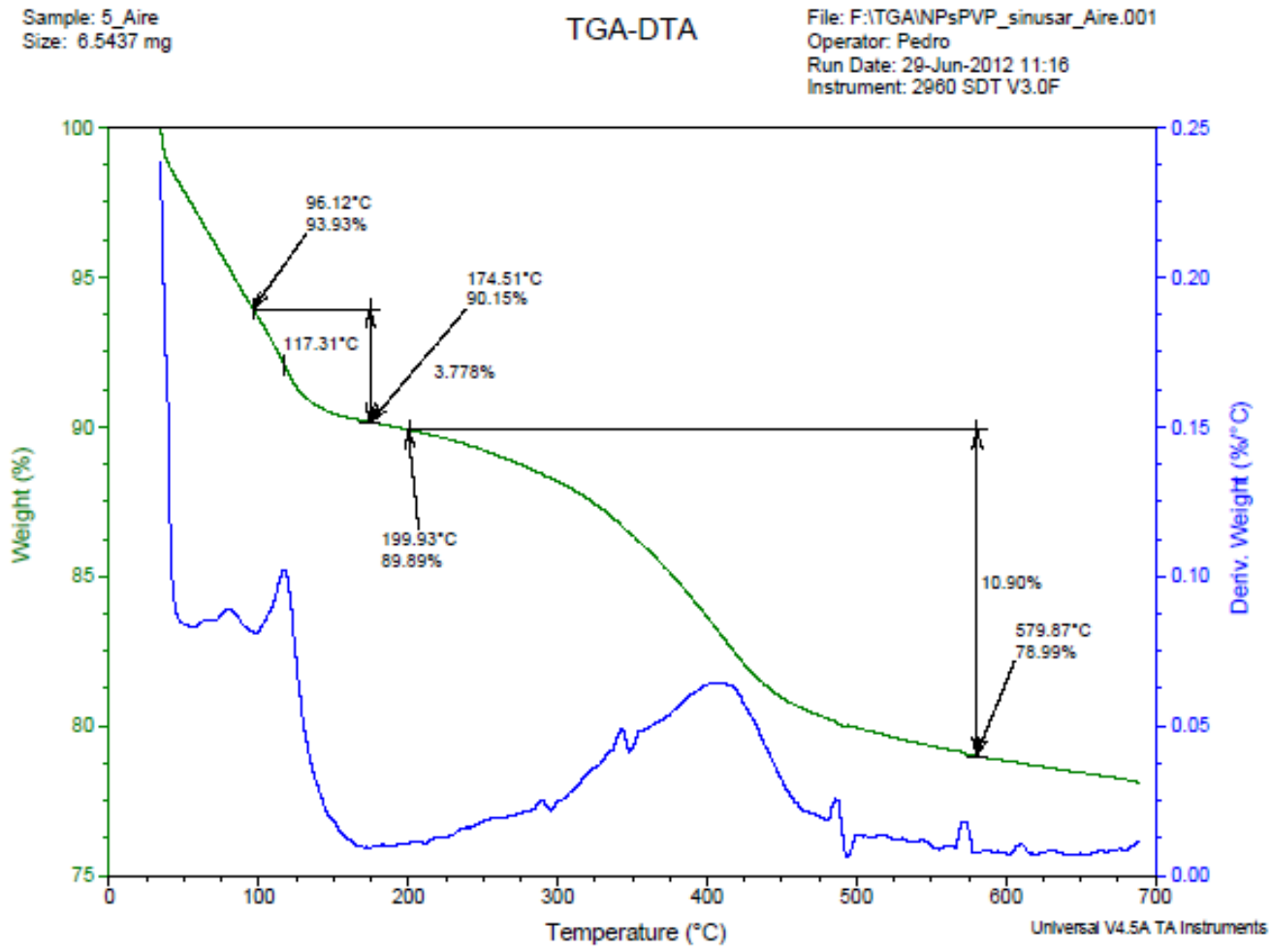

Fig. S6. TGA of freshly prepared Pd-PVP@[bmim][PF_6]-laponite catalyst

3.3 Exhaust Pd-PVP@ laponite catalyst applied to the reaction of iodobenzene with n-butyl acrylate

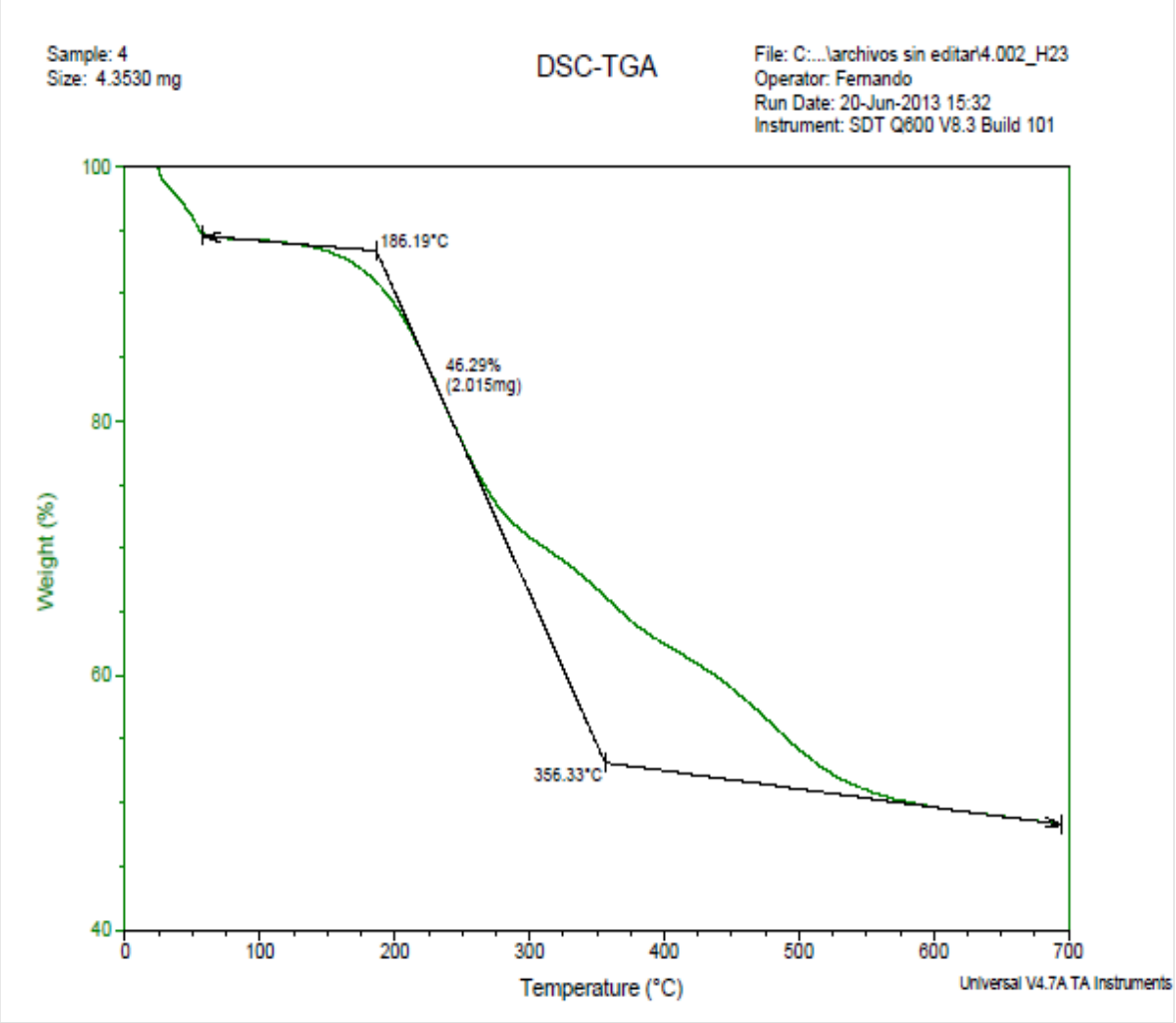

Fig. S7. TGA of the exhaust Pd-PVP@ laponite catalyst

3.4 Exhaust Pd-PVP@[bmim][PF_6]-laponite(0,1ml/g clay)catalyst applied to the reaction of iodobenzene with n-butyl acrylate

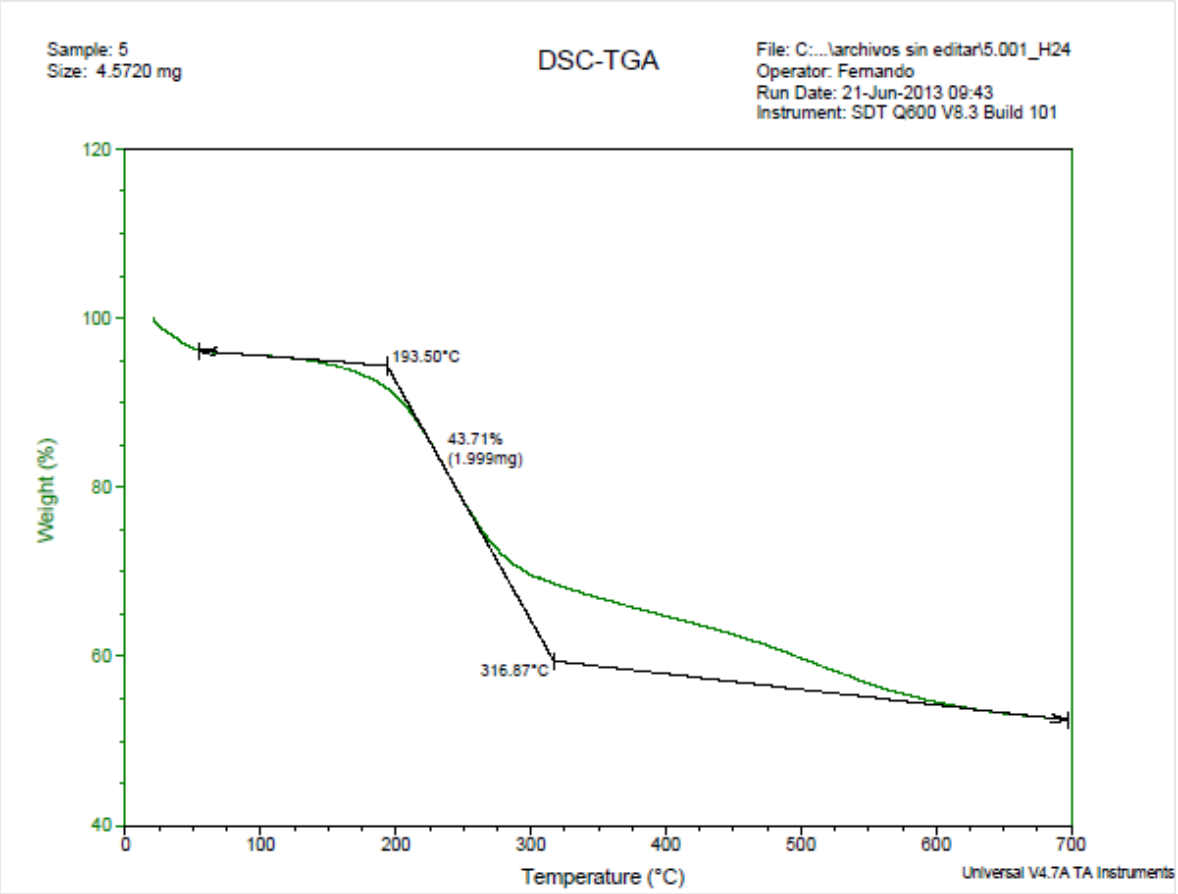

Fig. S8. TGA of the exhaust Pd-PVP@[bmim][PF_6]-laponite (0,1ml/g clay) catalyst

3.5 Exhaust Pd-PVP@[bmim][PF_6]-laponite (0,3ml/g clay) catalyst applied to the reaction of iodobenzene with n-butyl acrylate

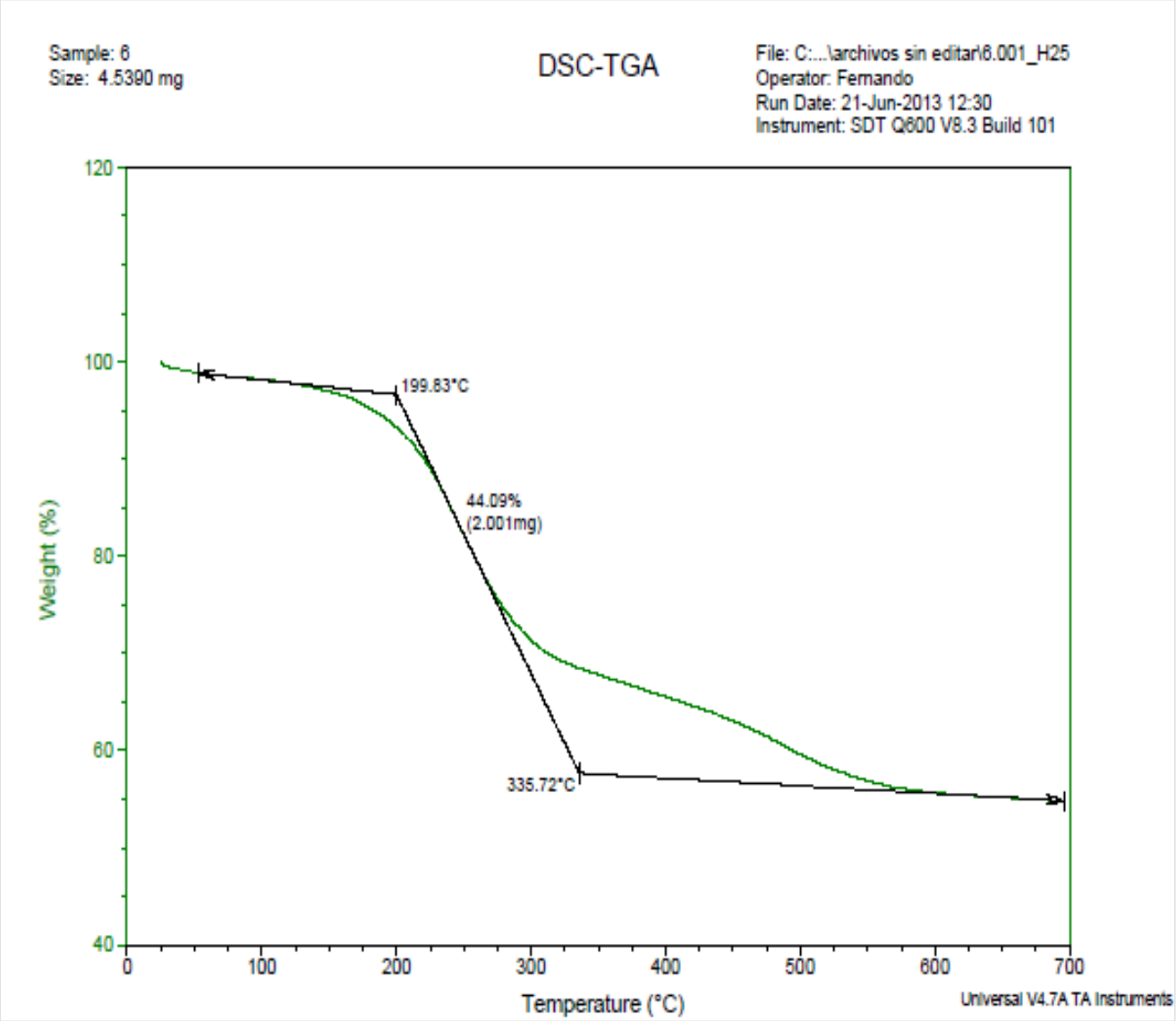

Fig. S9. TGA of the exhaust Pd-PVP@[bmim][PF_6]-laponite (0,3ml/g clay) catalyst

4. TEM analysis of the Catalytic Systems

4.1 TEM analysis of the freshly prepared catalyst

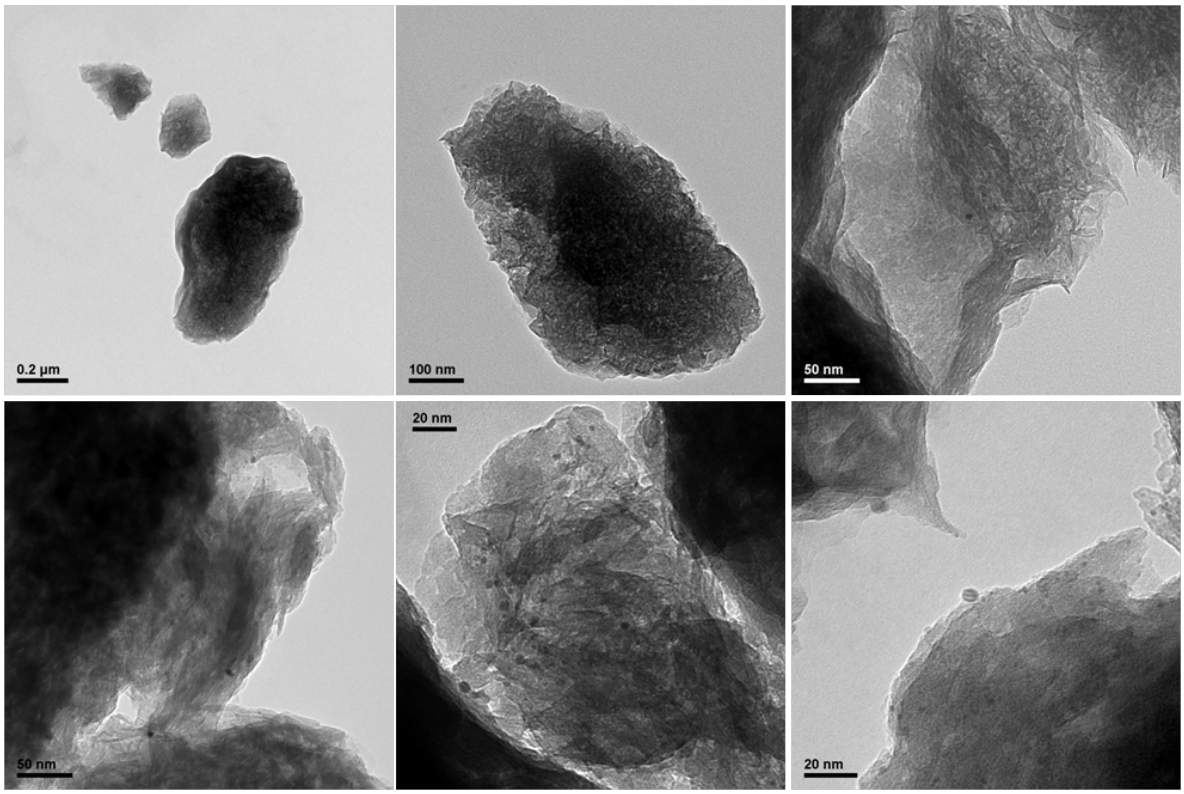

Fig. S10. TEM micrographs of the freshly prepared catalyst.

4.2 STEM analysis of the exhausted catalyst

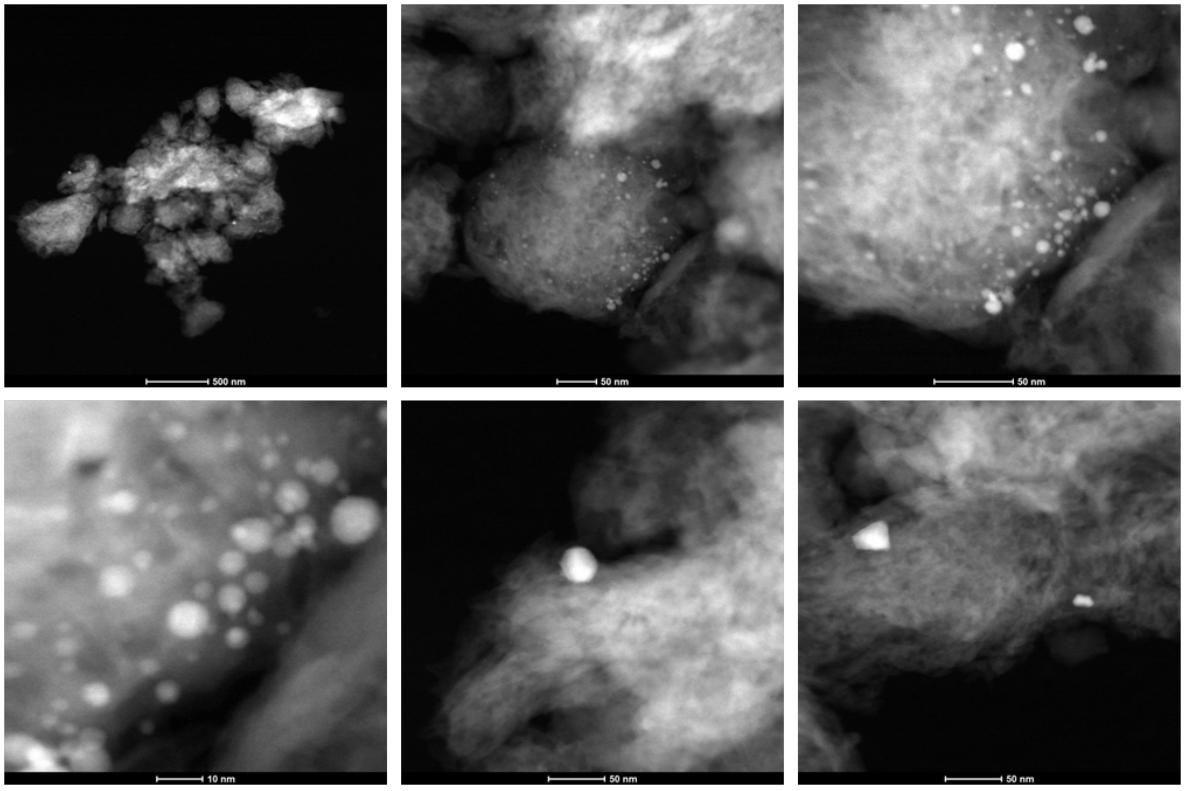

Fig. S11. STEM micrographs of the exhausted catalyst.

4.3 Size distribution of the supported Pd nanoparticles in a freshly prepared catalyst

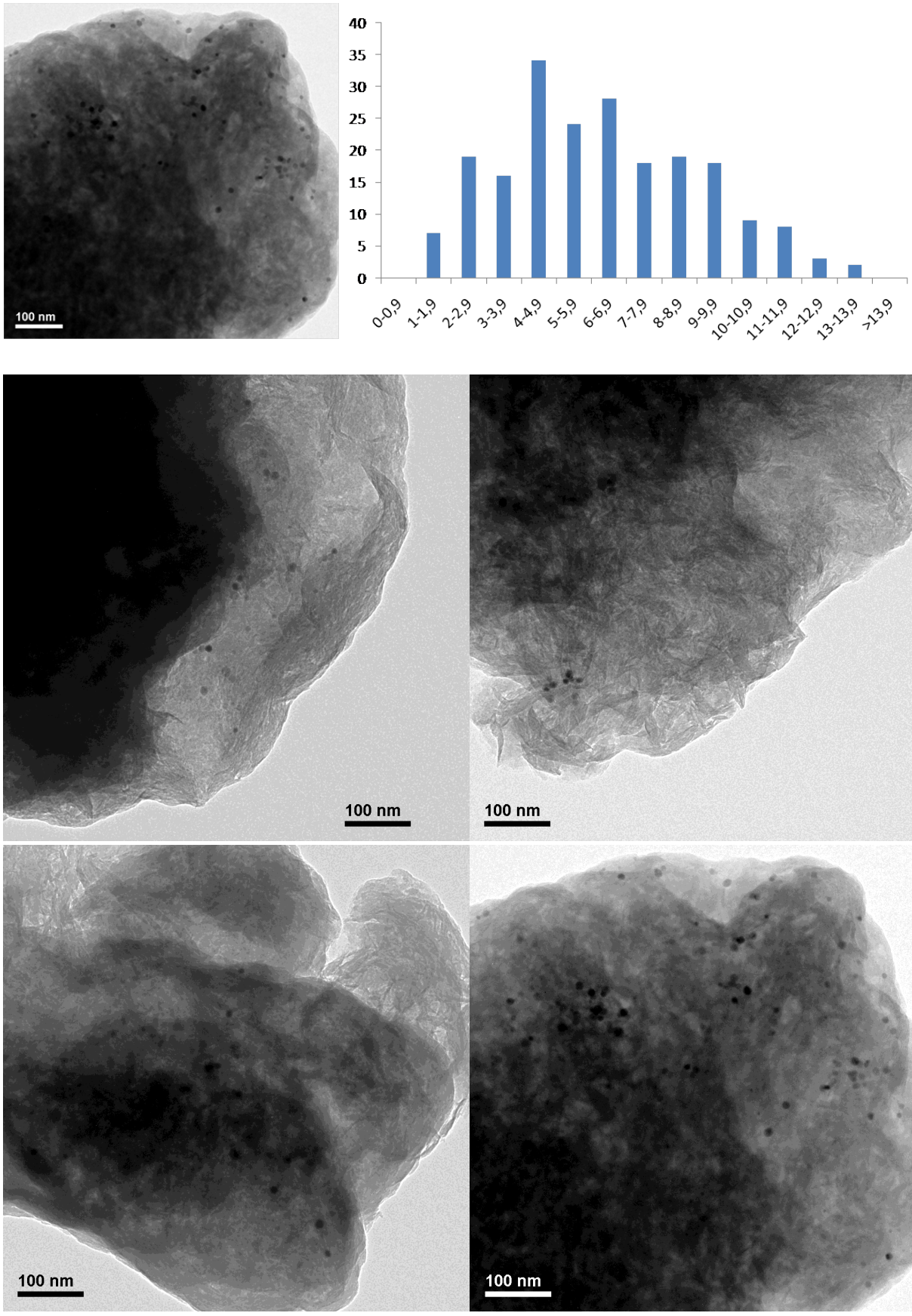

Fig. S12. Size distribution of the supported nanoparticles before use

5. FESEM analysis of the Catalytic Systems

5.1 Freshly prepared catalyst

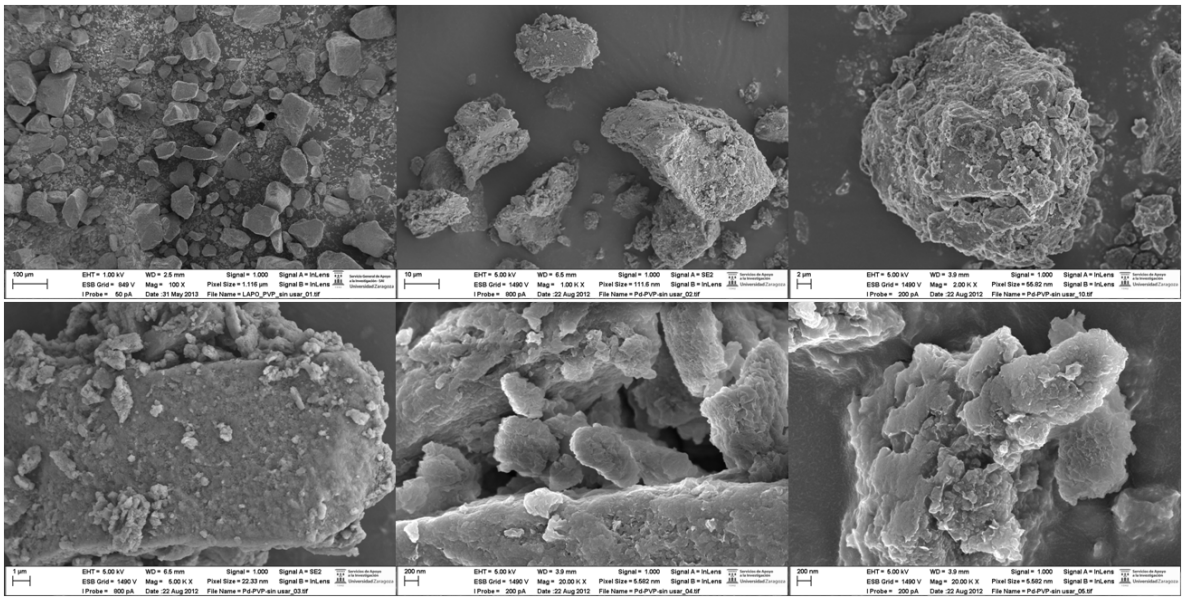

Fig. S13.FESEM micrographs of the freshly prepared catalyst

5.2 Exhausted catalyst

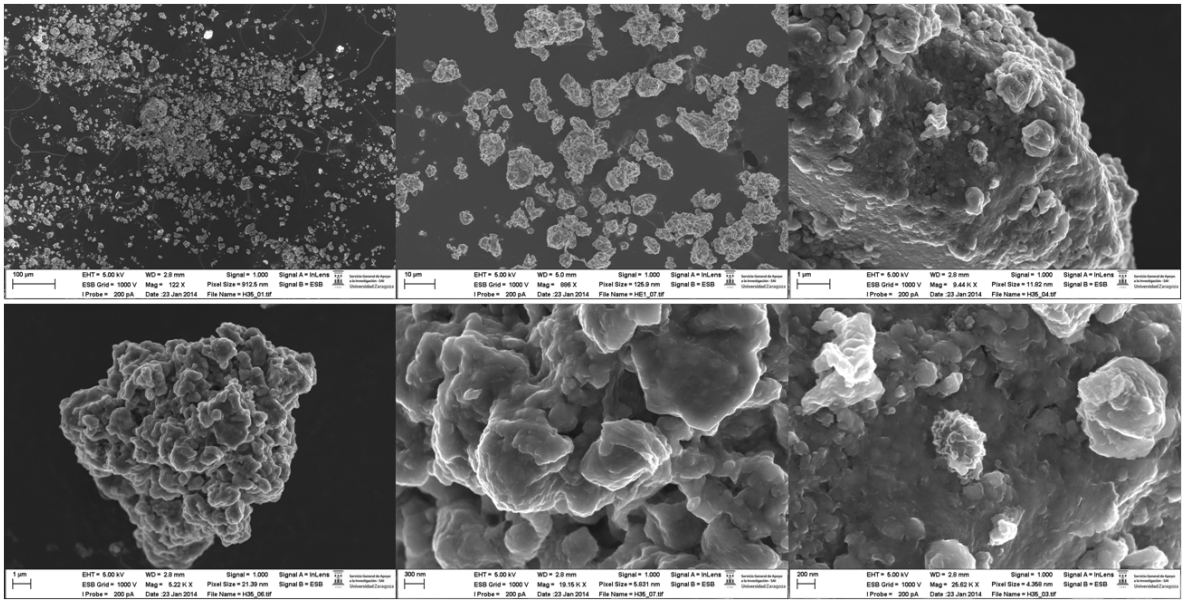

Fig. S14. FESEM micrographs of the exhausted catalyst

6. Complete results of recycling experiments

6.1 Heck coupling reaction of iodobenzene with n-butyl acrylate, using laponite-supported Pd nanoparticles, under microwave irradiation (at constant power).

Table S1. Results of Heck coupling reaction of iodobenzene with *n*-butyl acrylate, using laponite-supported Pd nanoparticles, under microwave irradiation.

Time(min)	Power(W)	Run	Iodobenzene conversion (%)	GC Product Yield (%)	Isolated Product Yield (%)
4	75	1	>99	>99	84
		2	60	54	40
		3	30	24	16
5	50	1	>99	>99	82
		2	95	93	60
		3	95	94	82
		4	70	60	44
		5	15	15	6
5	45	1	36	31	29
		2	95	94	81
		3	98	97	87
		4	79	72	53
5	40	1	50	45	41
		2	67	62	55
		3	89	87	73
		4	93	92	77
		5	95	94	68
		6	70	60	44
10	25	1	39	25	20
		2	96	94	72
		3	98	97	80
		4	95	90	68
		5	97	95	61
		6	86	84	73
		7	89	81	45
		8	85	82	68
		9	67	61	52
		10	76	69	53
		11	80	76	61
		12	57	10	5
5	50	1	91	87	61
5	25	2	67	60	50
		3	70	69	68
		4	79	76	66
		5	89	88	80
		6	52	43	36

6.2 Heck coupling reaction of iodobenzene with n-butyl acrylate, using laponite-supported Pd nanoparticles, under microwave irradiation (at constant temperature).

Table S2. Results of Heck coupling reaction of iodobenzene with *n*-butyl acrylate, using laponite-supported Pd nanoparticles, 10 minutes reaction time, under microwave irradiation (25 W) at constant temperature.

Temperature (ºC)	Run	Iodobenzene conversion (%)	GC Product Yield (%)	Isolated Product Yield (%)
80	1	42	39	36
	2	95	95	87
	3	96	96	89
	4	96	95	66
	5	94	93	74
	6	98	98	78
	7	86	77	46
	8	88	77	40
90	1	92	90	72
	2	94	94	91
	3	98	98	89
	4	97	97	87
	5	98	97	74
	6	98	98	76
	7	85	71	38
	8	79	69	48
100	1	80	78	73
	2	97	97	90
	3	97	97	85
	4	98	97	87
	5	97	97	91
	6	98	98	86
	7	85	74	41
	8	81	61	30
110	1	93	87	47
	2	97	97	89
	3	98	97	91
	4	98	97	56
	5	98	98	91
	6	83	74	49
	7	82	29	7

6.3 Heck coupling reaction of iodobenzene with n-butyl acrylate. using laponite supported Pd nanoparticles under microwave irradiation in the presence of [BMIM][PF$_6$]

Table S3. Results of Heck coupling reaction of iodobenzene with *n*-butyl acrylate using laponite-supported Pd nanoparticles, under microwave irradiation in the presence of [BMIM][PF$_6$].

[BMIM][PF$_6$] (ml/g clay)	Time (min)	Power (W)	run	Iodobenzene conversion (%)	GC Product Yield (%)	Isolated Product Yield (%)
0.3	5	30	1	82	80	74
			2	38	33	30
	5	25	1	94	92	77
			2	31	23	21
	10	15	1	52	49	46
			2	96	95	80
			3	83	79	63
			4	94	90	53
			5	97	95	52
			6	94	91	67
			7	98	96	60
			8	86	81	57
			9	90	88	73
			10	79	75	64
			11	72	68	59
			12	90	87	66
			13	86	81	62
			14	17	17	6
0.1	5	45	1	91	91	87
			2	92	90	75
			3	91	89	73
			4	13	10	7
	5	40	1	86	84	72
			2	93	91	73
			3	89	87	73
			4	92	89	62
			5	89	81	45
			6	n.d	n.d	n.d
	5	35	1	49	45	42
			2	76	74	70
			3	97	97	74
			4	91	90	80
			5	4	6	1
	10	20	1	70	69	66
			2	98	97	81
			3	95	89	38
			4	94	89	52
			5	96	94	63
			6	90	88	79
			7	92	90	65
			8	86	83	68
			9	70	66	58
			10	57	39	28
			11	74	65	49
			12	64	42	26
			13	60	31	18
			14	5	8	3

6.4 Heck coupling reaction of iodobenzene with n-butyl acrylate, using laponite-supported Pd nanoparticles, under microwave irradiation in the presence of tetrabutylammonium bromide (TBAB)

Table S4. Results of Heck coupling reaction of iodobenzene with *n*-butyl acrylate, using laponite-supported Pd nanoparticles, under microwave irradiation in the presence of TBAB.

TBAB (mmol/g clay)	Time(min)	Power(W)	run	Iodobenzene conversion (%)	GC Product Yield (%)	Isolated Product Yield (%)
1.46	5	25	1	>99	>99	95
			2	98	98	90
			3	98	98	88
			4	97	97	80
			5	97	96	79
			6	96	96	77
			7	97	96	87
			8	63	60	59
			9	38	38	34
			10	6	6	5
	10	15	1	>99	>99	81
			2	>99	>99	66
			3	85	83	74
			4	48	45	42
	5	20	1	92	92	87
			2	28	19	17
			3	20	9	8
			4	40	36	29
0.48	5	40	1	91	89	72
			2	93	92	79
			3	93	92	87
			4	96	96	80
			5	80	69	45
			6	32	30	15
	10	20	1	70	66	60
			2	95	95	88
			3	87	86	81
			4	60	54	47
			5	60	54	36
			6	28	25	17
	5	40	1	92	91	84
		20	2	64	61	57
			3	62	58	54
			4	71	70	67