

Figure S1: Survey spectra of A) bare GNP, B) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, C) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, D) w-Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, E) w-Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, F) w-Pd/GNP<sub>0.5</sub>-EtOH-fast, G) w-Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, H) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, I) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow

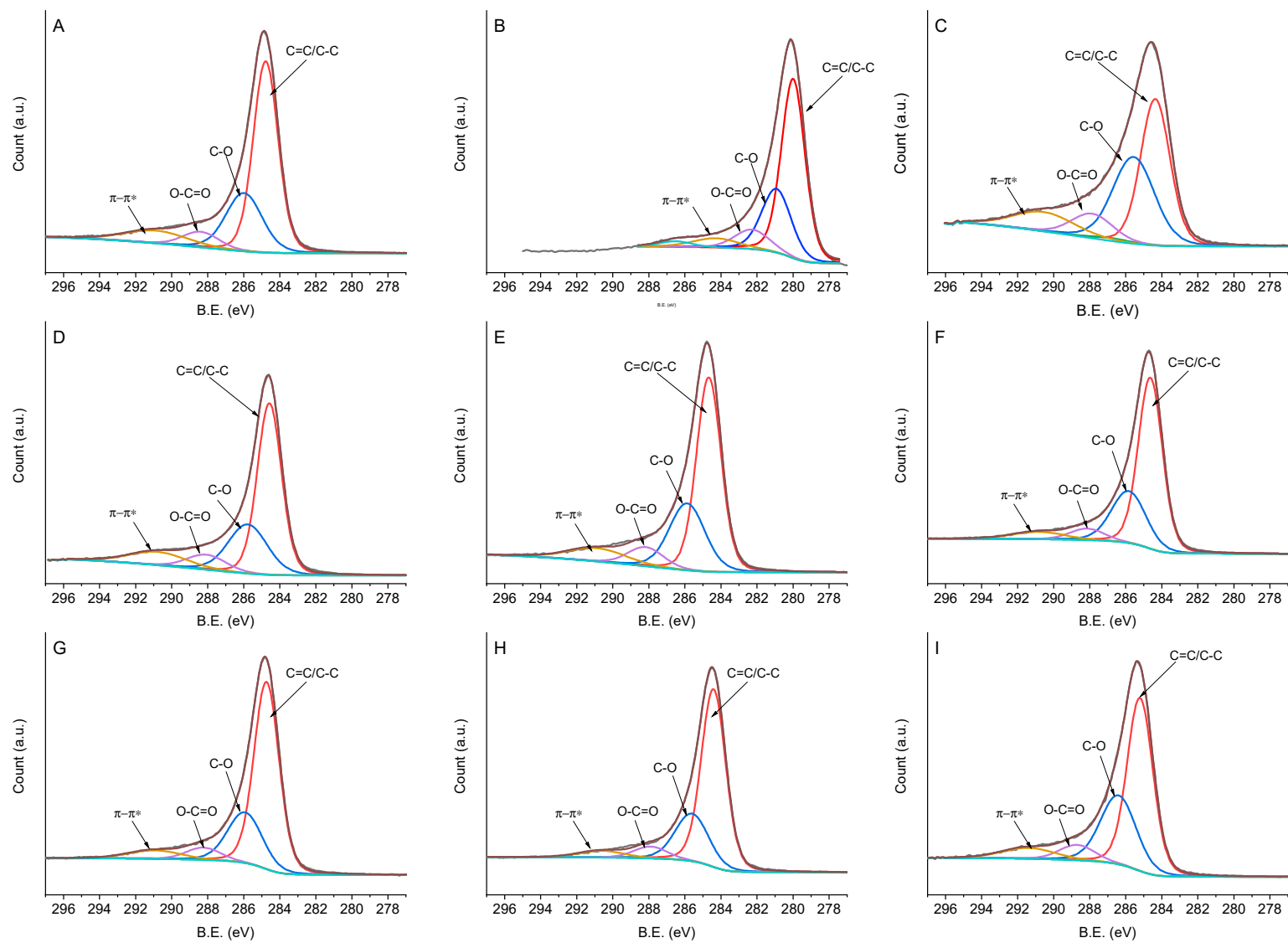


Figure S2: C1s region of A) bare GNP, B) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, C) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, D) w-Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, E) w-Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, F) w-Pd/GNP<sub>0.5</sub>-EtOH-fast, G) w-Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, H) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, I) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow

Table S1: Results of the XPS analysis.

		Survey						C 1s				
		C	O	Cl	Pd	O/C	Pd/C	C=C/C-C	C-O	C=O	O=C-O	p-p*
GNP	<i>B.E. (eV)</i>	284.50	532.50	-				284.78	285.98	287.28	288.38	290.88
	% At.	94.7	5.3	-	-	0.056	-	57.8	25.6	0	6.8	9.7
Pd/GNP <sub>0.5</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.60	532.60	17.5				284.61	285.96	287.17	288.11	290.84
	% At.	92.1	7.8	0.10	0.16	0.084	0.0017	42.0	35.2	1.2	9.9	11.7
w-Pd/GNP <sub>0.5</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.13	533.13	-	341.13			284.65	285.9	287.15	288.05	290.85
	% At.	93.2	6.2	-	0.55	0.066	0.0059	51.3	26.7	0	7.3	14.7
Pd/GNP <sub>0.2</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.75	533.75	17.7	335.75			284.63	285.86	287.21	288.12	290.54
	% At.	93.9	5.8	0.12	0.21	0.062	0.0022	56.4	25.9	0	7.6	10.1
w-Pd/GNP <sub>0.2</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.95	532.95	-	335.95			284.58	285.78	287.08	288.08	290.77
	% At.	93.8	5.7	-	0.55	0.061	0.0059	56.1	25.8	0	7.9	10.3
Pd/GNP <sub>1.0</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.60	532.60	17.6	336.6			284.61	285.37	286.89	289.42	290.43
	% At.	93.0	6.5	0.09	0.41	0.069	0.044	51.7	31.2	1.4	7.9	7.8
w-Pd/GNP <sub>1.0</sub> -H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.38	532.38	-	336.38			284.67	285.88	287.18	288.17	290.87
	% At.	94.1	5.6	-	0.27	0.059	0.0029	57.8	26.2	0.1	7.2	8.8
Pd/GNP <sub>0.5</sub> -EtOH-fast	<i>B.E. (eV)</i>	284.6	532.6	17.6	335.6			284.60	285.36	286.77	288.73	290.23
	% At.	91.7	7.7	0.11	0.49	0.083	0.0053	53.2	34.7	2.2	6.2	3.7
w-Pd/GNP <sub>0.5</sub> -EtOH-fast	<i>B.E. (eV)</i>	284.43	532.43	-	335.4			284.63	285.83	287.14	288.14	290.83
	% At.	93.9	5.6	-	0.53	0.059	0.0056	61.4	26.8	0.2	5.9	5.7
w-Pd/GNP <sub>0.5</sub> -EtOH/H <sub>2</sub> O-fast	<i>B.E. (eV)</i>	284.58	532.58	-	335.58			284.73	285.93	287.23	288.23	290.93
	% At.	94.1	5.5	-	0.37	0.058	0.0039	64.0	23.9	0.2	5.8	6.1
w-Pd/GNP <sub>0.5</sub> -H <sub>2</sub> O-medium	<i>B.E. (eV)</i>	284.46	532.46	-	335.46			284.41	285.61	286.92	287.89	290.61
	% At.	92.1	7.4	-	0.37	0.080	0.0040	65.5	24.1	0	5.9	4.5
w-Pd/GNP <sub>0.5</sub> -H <sub>2</sub> O-slow	<i>B.E. (eV)</i>	284.25	532.25	-	336.25			285.21	286.4	287.71	288.68	291.42
	% At.	93.8	5.8	-	0.45	0.061	0.0048	55.5	30.6	0	7.0	7.2

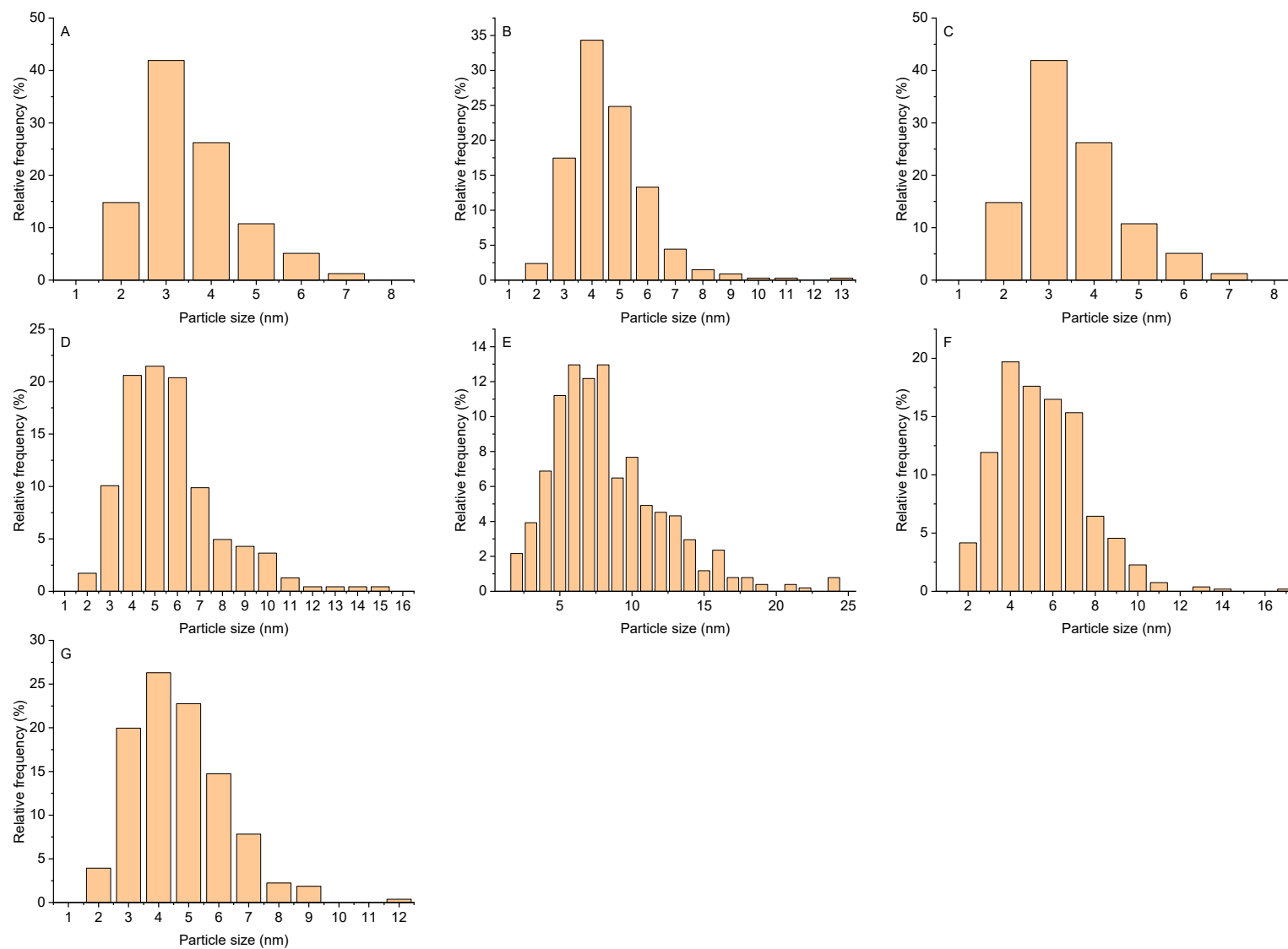


Figure S3: Particle size distribution obtained from TEM analyses of A) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, B) w-Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, C) w-Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, D) w-Pd/GNP<sub>0.5</sub>-EtOH-fast, E) w-Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, F) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, G) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow catalysts.

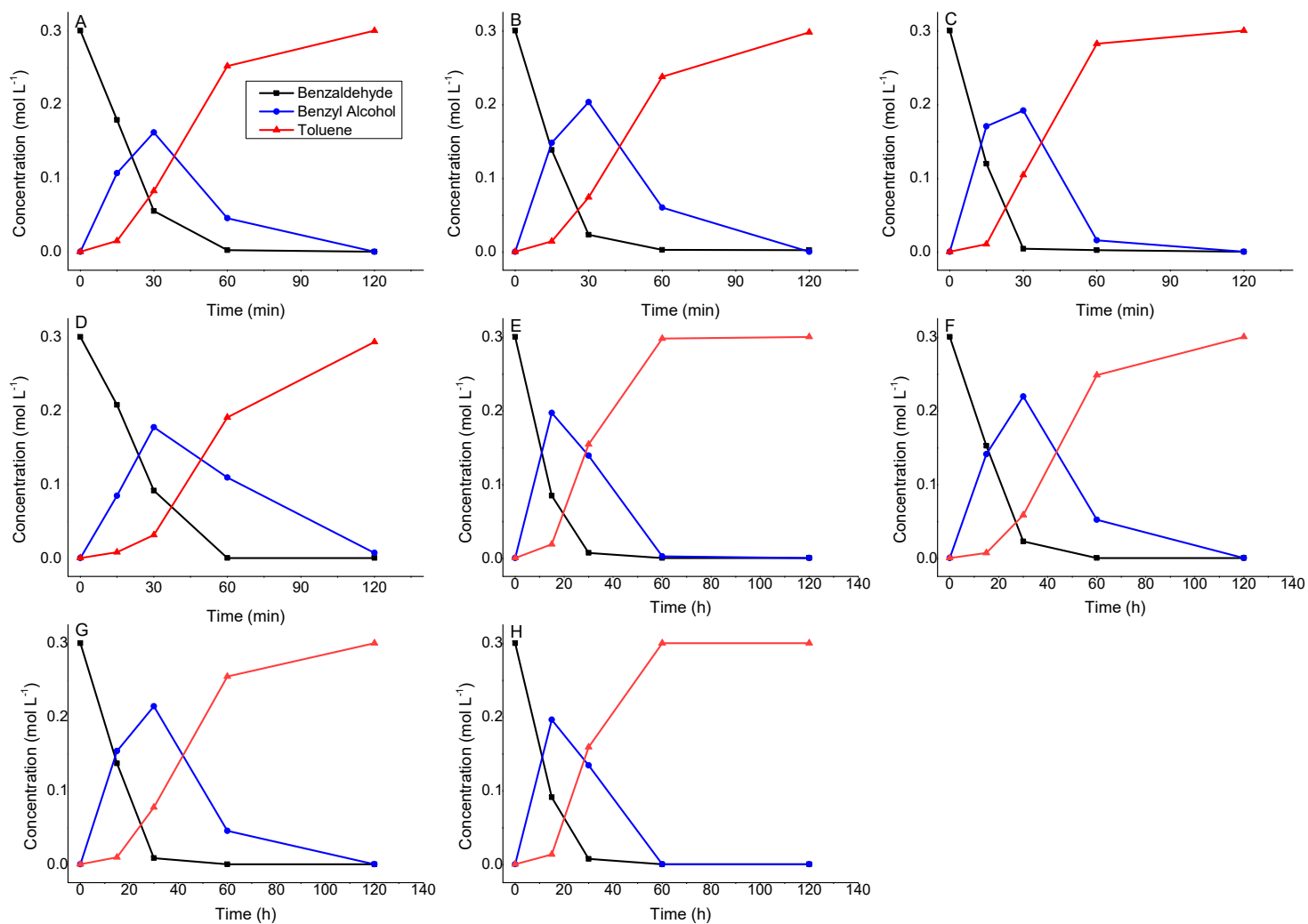


Figure S4: Reaction profile using A) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, B) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, C) w-Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, D) w-Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, E) w-Pd/GNP<sub>0.5</sub>-EtOH-fast, F) w-Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, G) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, H) w-Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow catalysts.

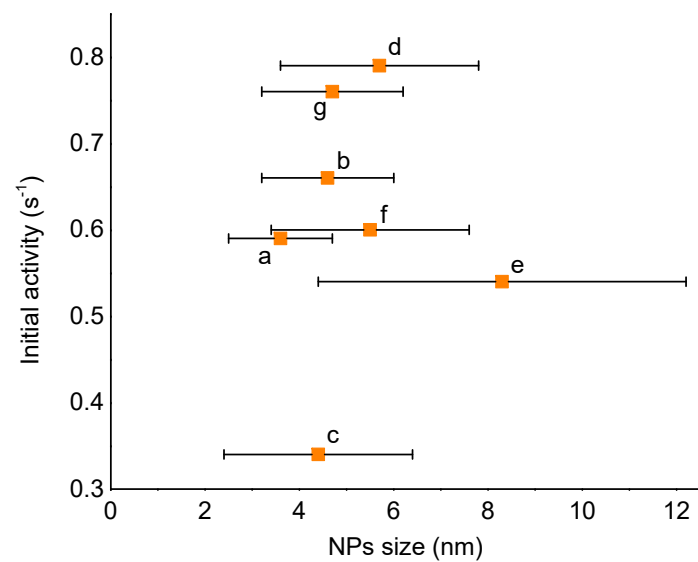


Figure S5: Influence of NPs size on the initial activity of the different catalysts: (a) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, (b) Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, (c) Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, (d) Pd/GNP<sub>0.5</sub>-EtOH-fast, (e) Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, (f) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, (g) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow.

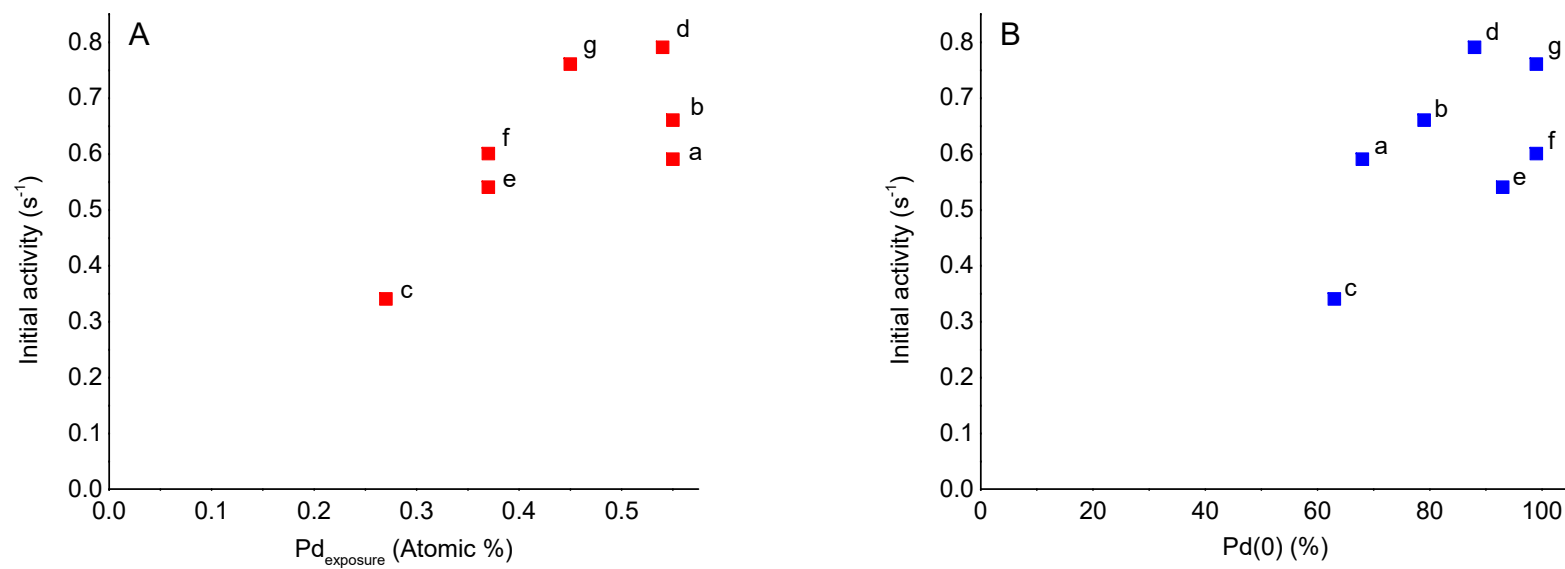


Figure S6: Influence of the A) Pd exposure and B) Pd(0) amount on the activity of the different catalysts: (a) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-fast, (b) Pd/GNP<sub>0.2</sub>-H<sub>2</sub>O-fast, (c) Pd/GNP<sub>1.0</sub>-H<sub>2</sub>O-fast, (d) Pd/GNP<sub>0.5</sub>-EtOH-fast, (e) Pd/GNP<sub>0.5</sub>-EtOH/H<sub>2</sub>O-fast, (f) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-medium, (g) Pd/GNP<sub>0.5</sub>-H<sub>2</sub>O-slow.