Supplementary Materials

Adsorption Behavior and Electron Structure Engineering of Pd-Based Catalysts for Acetylene Hydrochlorination

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Received: 17 November 2019; Accepted: 20 December 2019; Published: 24 December 2019

Table S1. The comparisons of catalytic performance of various catalysts reported in literatures.

References	Site Time Yield (STY) (kg_{VCM} kg_{Cat}^{-1} h^{-1}))
[1]	0.01201
[2]	0.40306
[3]	0.05648
[4]	1.4305
[5]	0.20753
[6]	0.06262
[7]	0.15693
[8]	0.04958
[9]	0.01815
[10]	0.2267
[11]	1.29785
[12]	0.01815
[13]	1.83995
[14]	0.04958
[15]	0.5104
[16]	1.86525
[17]	0.85084
[18]	1.3799
[19]	0.03732
[20]	3.22

[21]	0.039
[22]	0.35394
[23]	0.06567
[24]	0.30283
[25]	0.30254
[26]	0.37399
[27]	0.37195
[28]	0.36954
[29]	0.35576
[30]	0.51
[31]	1.8161
This work	2.3

[a] STY (kg_{VCM} kg_{Cat}^{-1} h^{-1}) was calculated as the average conversion of acetylene when the reaction reached steady state.

Table S2. Parameters for the C_2H_2 and HCl molecules adsorption on Pd-based catalysts: adsorption energy (E_{ads}), bond length of the adsorbed molecule (d_{C-C} or d_{H-Cl}).

Catalysts	Bond length /Å		$E_{ads}(C_2H_2)$ kJ/mol	E_{ads}(HCl) kJ/mol	$\lvert E_{ads}(C_2H_2)-E_{ads}(HCl)\rvert$ kJ/mol
	d_{C-C}	d_{H-Cl}			
Pd/AC	1.224	1.310	-125.02	-64.65	60.37
Pd-A/AC	1.219	1.374	-46.01	-85.26	39.25
Pd-IL/AC	1.217	1.292	-29.75	-14.46	15.29
Pd-A-IL/AC	1.216	1.319	-26.28	-42.75	16.47
Pd-EDA-IL/AC	1.208	1.305	-24.8	-60.79	35.99
Pd-PR-IL/AC	1.212	1.295	-34.55	-15.37	19.18
Pd-PD-IL/AC	1.215	1.311	-64.75	-19.16	45.59

Table S3. Parameters for the C_2H_2 and HCl molecules adsorption on Pd-based catalysts: Hirshfeld charge (CH), bond length of the adsorbed molecule ($d_{C\text{-}C}$ or $d_{H\text{-}Cl}$).

Samples	C_H(Pd)		C_H(N)		Bond length /Å	
	Without C_2H_2	With C_2H_2	Without C_2H_2	With C_2H_2	$d_{C\text{-}C}$	$d_{H\text{-}Cl}$
Pd-A	0.334	0.293	-0.083 -0.093	-0.108 -0.113	1.224	1.310
Pd-A-IL	0.359	0.365	-0.105 -0.090	-0.107 -0.105	1.216	1.319
Pd-EDA-IL	0.356	0.368	-0.177 -0.047 -0.053 -0.189	-0.210 -0.136 -0.149 -0.208	1.208	1.305
Pd-PR-IL	0.360	0.363	-0.014 -0.017	-0.017 -0.016	1.212	1.295
Pd-PD-IL	0.354	0.380	-0.010 -0.014	-0.018 -0.016	1.215	1.311

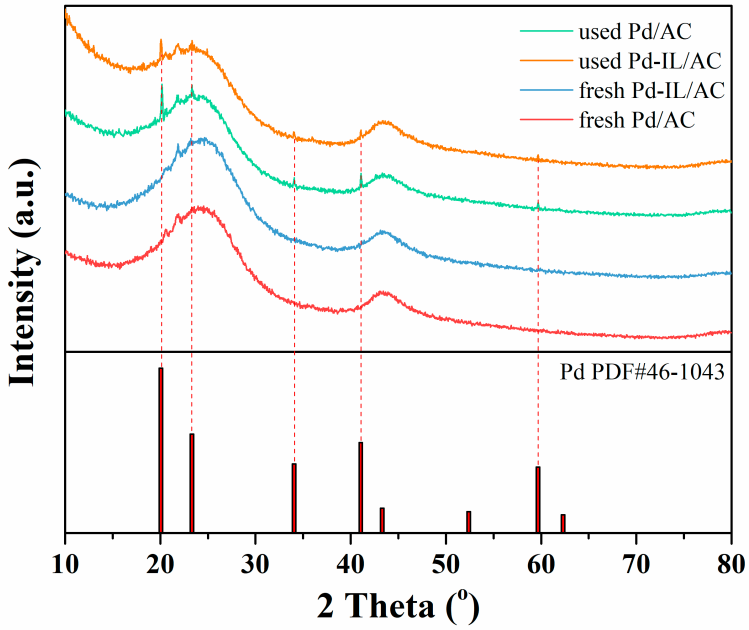

Figure S1 XRD results of fresh and used Pd/AC and Pd-IL/AC catalysts.

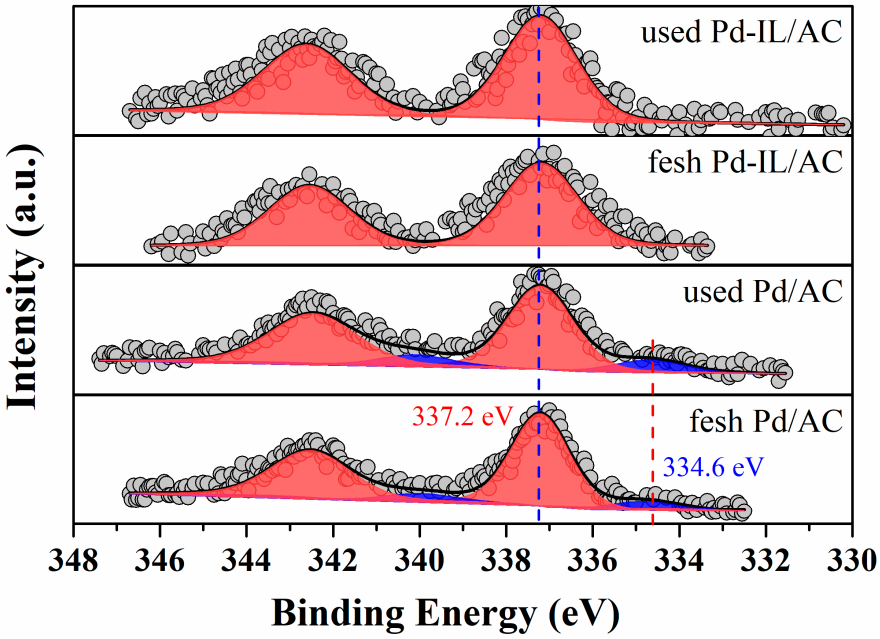

Figure S2 XPS spectra of fresh and used Pd/AC and Pd-IL/AC catalysts.

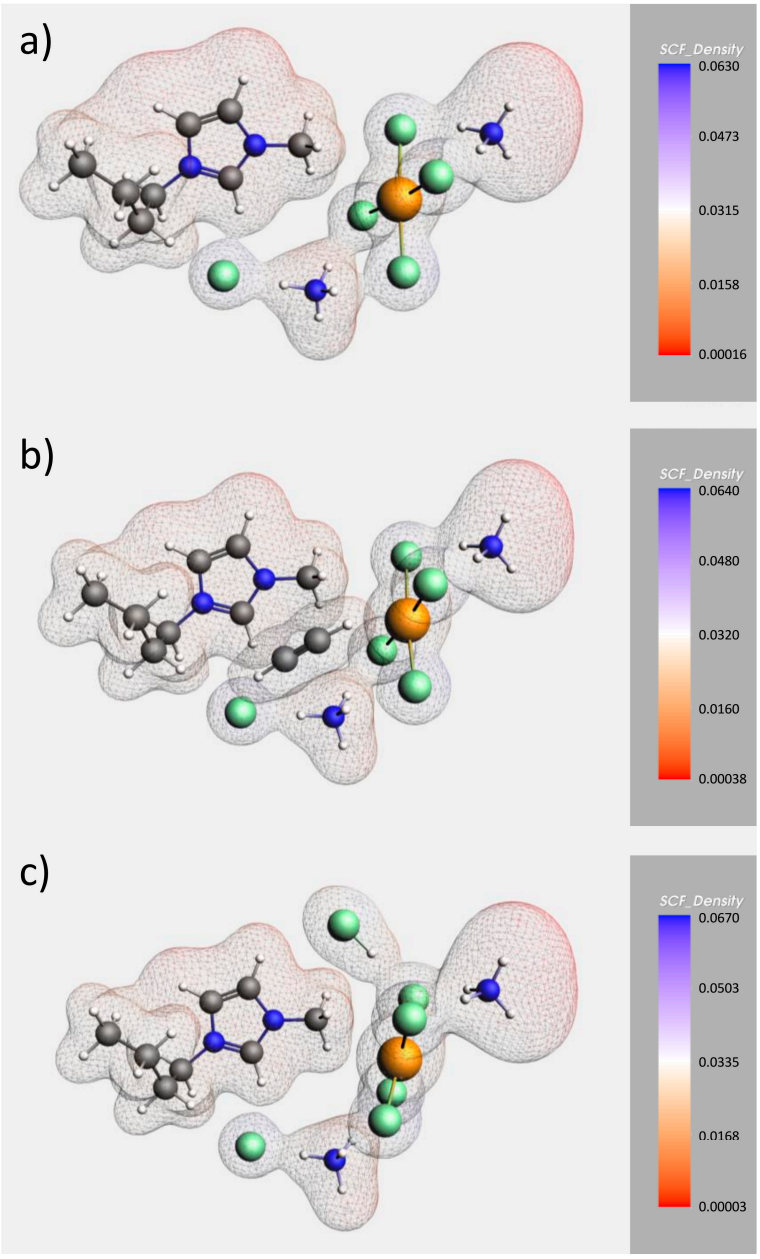

Figure S3. The electron density of a) Pd-2A-IL; b) Pd-2A-IL-C_2H_2; c) Pd-2A-IL-HCl.

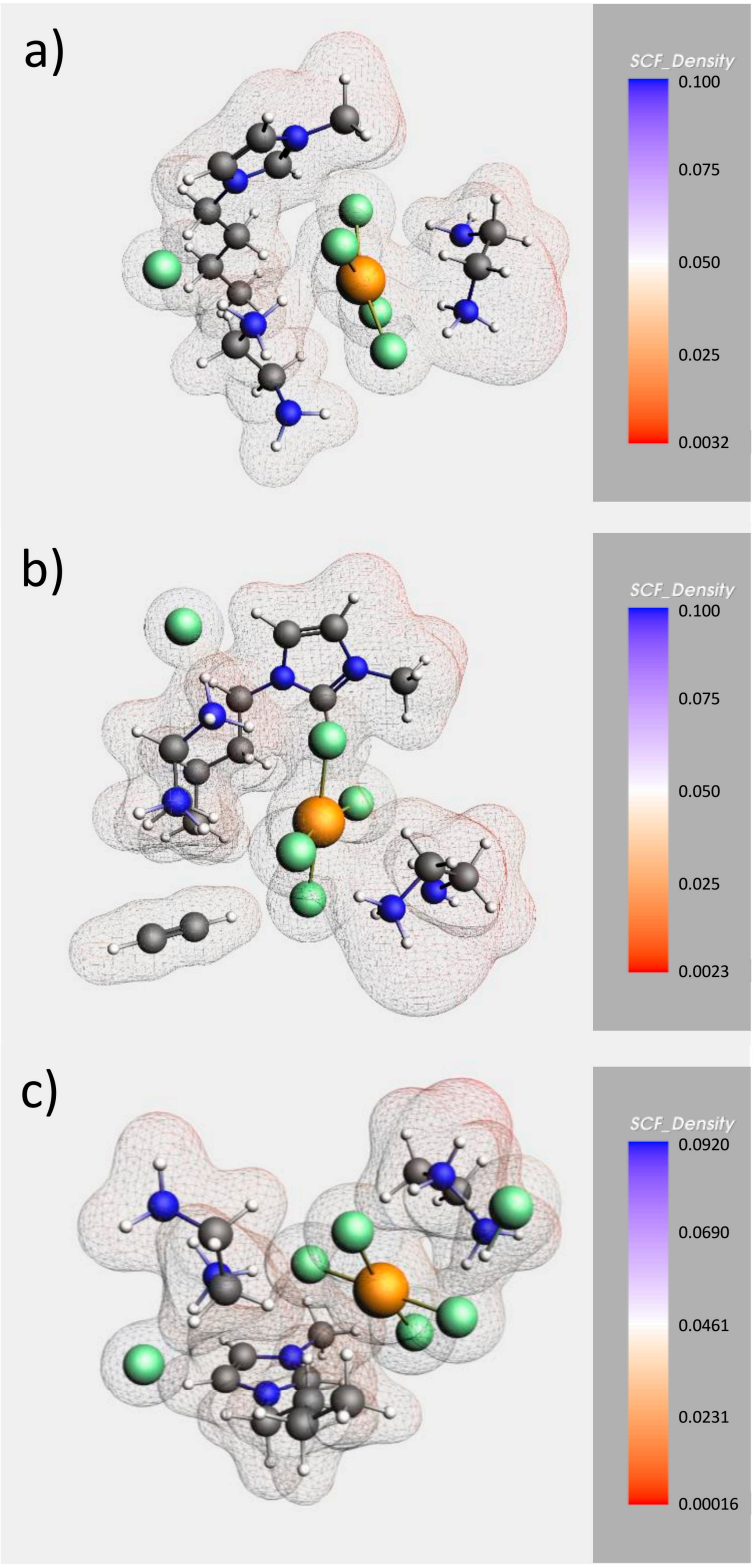

Figure S4. The electron density of a) Pd-2EDA-IL; b) Pd-2EDA-IL-C_2H_2; c) Pd-2EDA-IL-HCl.

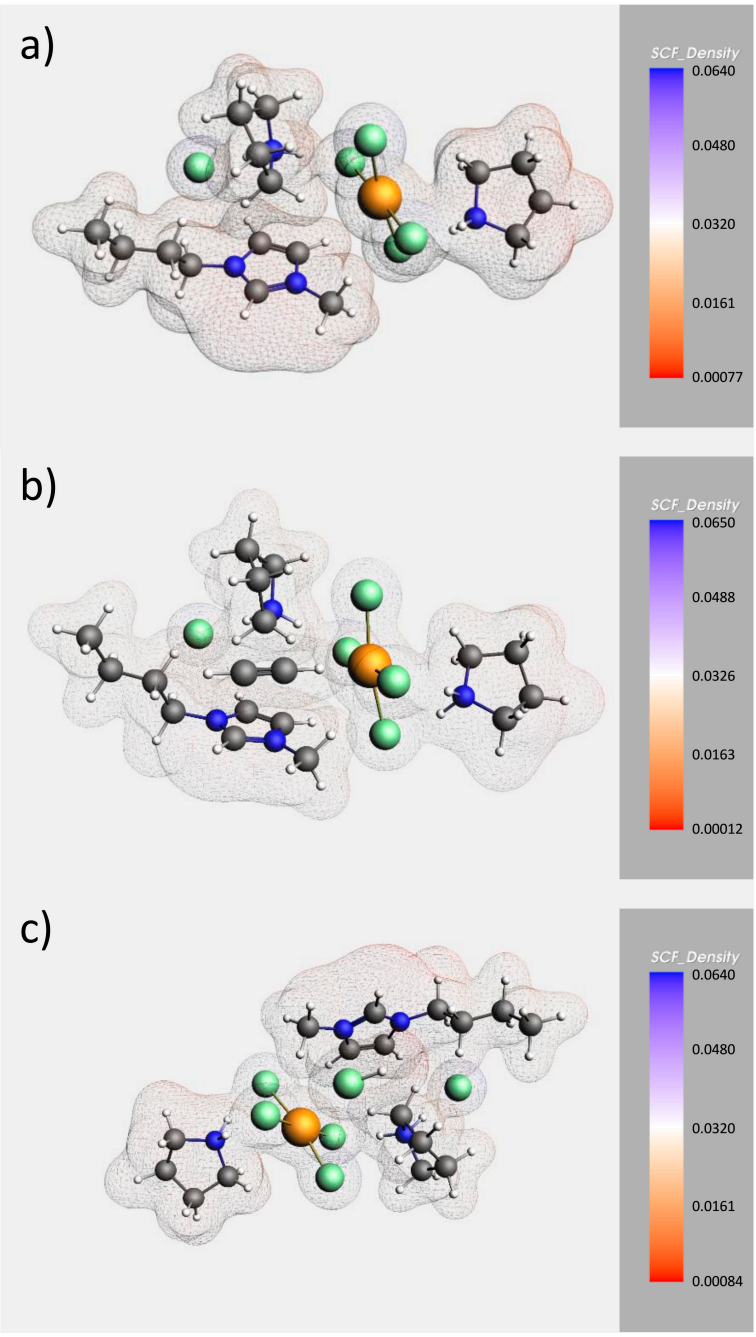

Figure S5. The electron density of a) Pd-2PR-IL; b) Pd-2PR-IL-C_2H_2; c) Pd-2PR-IL-HCl.

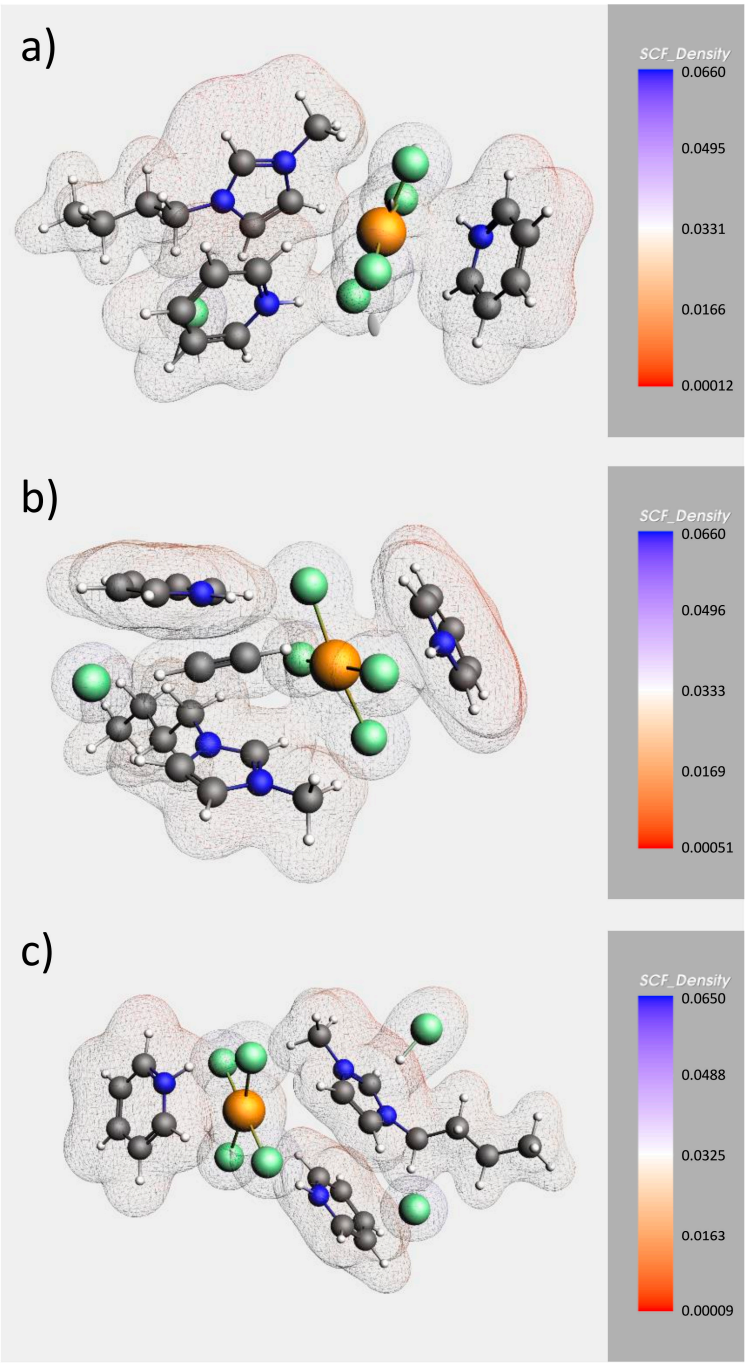

Figure S6. The electron density of a) Pd-2PD-IL; b) Pd-2PD-IL-C_2H_2; c) Pd-2PD-IL-HCl.

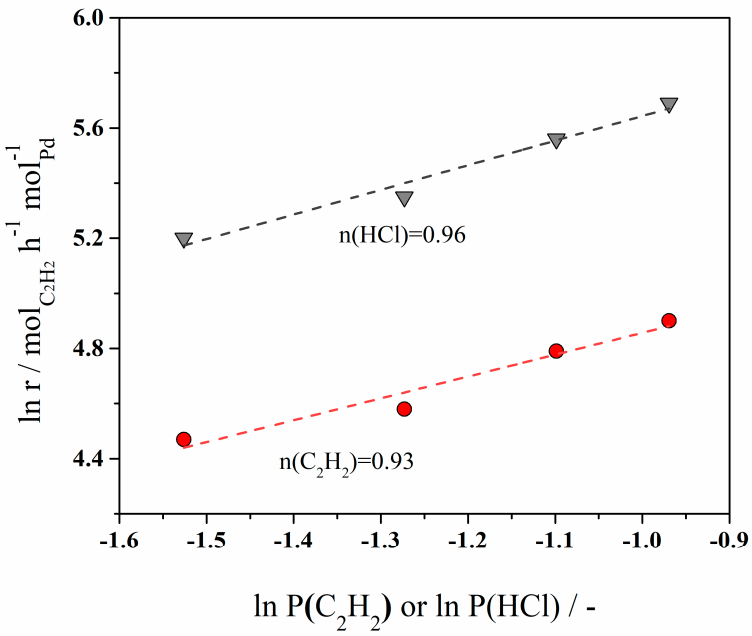

Figure S7 Reaction orders for HCl and C_2H_2 over Pd-2A-IL/AC (Calculated at <15% conversion of acetylene).

The linear dependence of both HCl and C_2H_2 reaction rate, as shown in Figure S7, demonstrates first-order dependence with respect to each reactant and second-order reaction kinetics overall, which may indicate a concerted HCl and C_2H_2 addition to the Pd-A-IL active site.

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