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Electronic Supplementary Information

Identification of Hydrogen Species on Pt/Al_2O_3 by *in situ* Inelastic Neutron Scattering and their Reactivity with Ethylene

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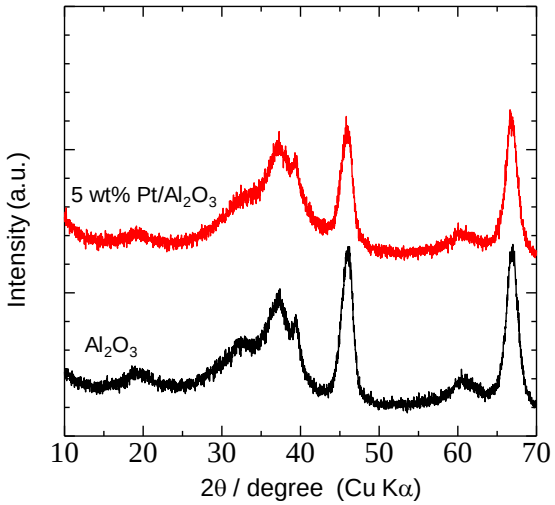


Figure S1. XRD patterns of 5wt% Pt/Al_2O_3 and the bare Al_2O_3.

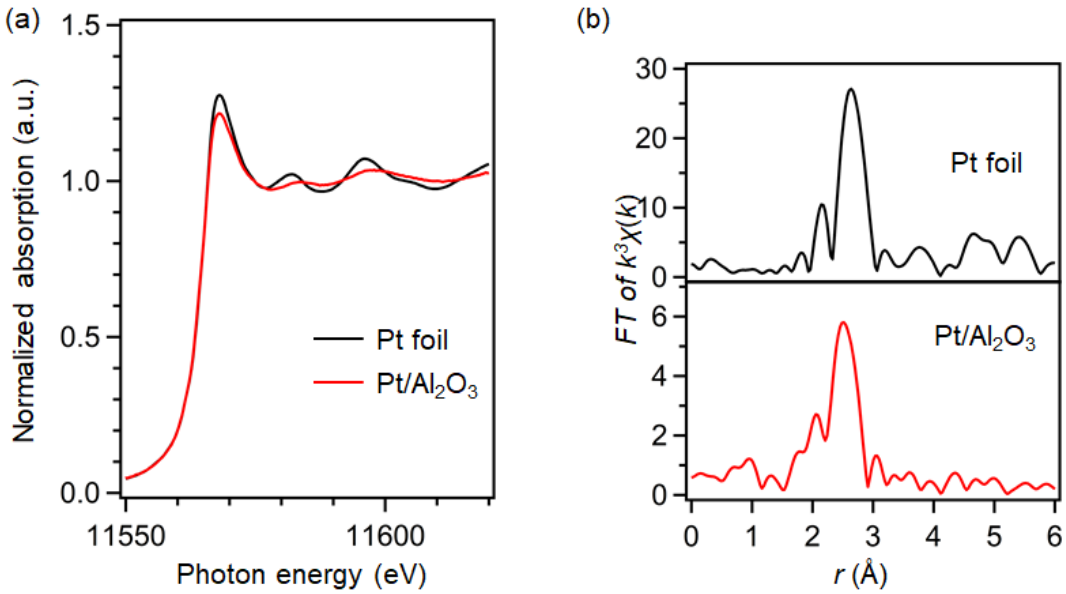


Figure S2. Pt L_3-edge (a) XANES and (b) FT-EXAFS spectra of 5wt% Pt/Al_2O_3 and Pt foil.

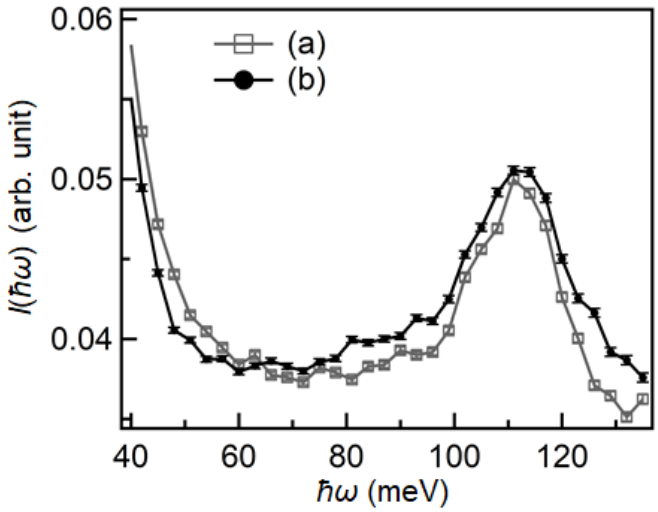
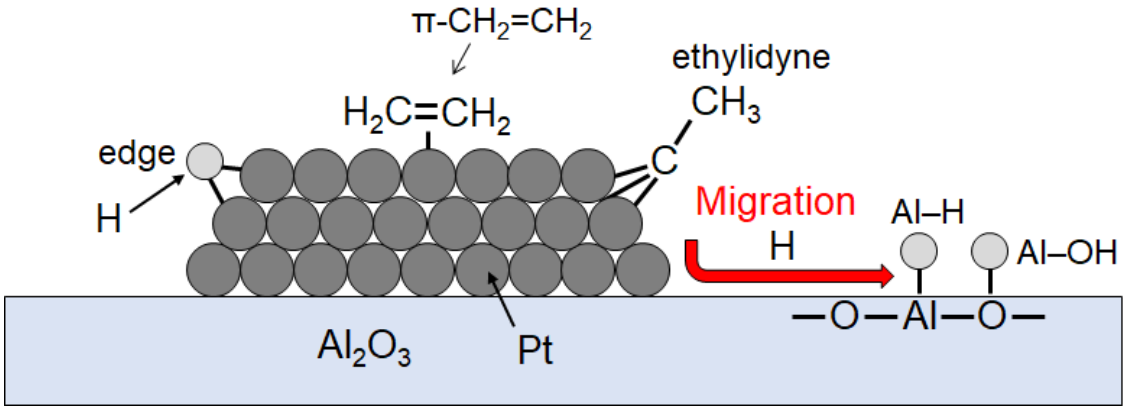


Figure S3. Inelastic neutron scattering spectra of (a) Al_2O_3 support with 5%H_2 (He balance), (b) the 5wt% Pt/Al_2O_3 sample with He.



Scheme S1. Formation mechanism of surface species on Pt/Al_2O_3 in the presence of C_2H_2.

Table S1. Curve fitting results of Pt L_3-edge FT-EXAFS of 5wt%Pt/Al_2O_3 and Pt foil

Sample	Neighbor atom	*CN*[a]	*r* (Å)[b]	DW[c]	R factor[d]
5wt% Pt/Al_2O_3	Pt	5.7±0.3	2.66±0.03	0.009±0.004	5.9
Pt foil	Pt	12.4±0.3	2.76±0.01	0.005±0.001	12.2

[a] Coordination number, [b] bond length, [c] Debye-Waller factor,
[d] $R = (\Sigma(k^3\chi^{data}(k)–k^3\chi^{fit}(k))^2)^{1/2}/(\Sigma(k^3\chi^{data}(k))^2)^{1/2}$

Table S2. Atomic coordinates of ten H adsorbed Pt_{14} $(Al_2O_3)_{16}$

Atom	x	y	z
Al	8.794862	4.241624	0.457553
Al	0.803466	4.259209	0.463587
Al	8.017248	1.416540	1.416145
Al	0.025867	1.445739	1.438879
Al	5.852140	4.242486	1.461283
Al	13.843613	4.248283	1.469647
Al	2.949676	-0.059102	1.510967
Al	10.941139	-0.053315	1.519321
Al	2.942069	2.886581	1.501568
Al	10.933552	2.892348	1.509932
Al	12.980235	1.415198	2.763096
Al	4.986366	1.415495	2.794609
Al	12.066311	4.244612	4.228139
Al	15.046874	2.870779	4.233356
Al	15.075348	-0.022947	4.209462
Al	9.978559	1.445443	4.305356
Al	7.048763	2.849517	4.233753
Al	7.064850	-0.021993	4.229441
Al	4.099180	4.221144	4.257870
Al	1.990483	1.428155	4.306937
Al	1.058176	4.242627	5.602389
Al	9.046951	4.247239	5.620337
Al	5.034776	1.413224	5.799601
Al	13.057875	1.368416	5.741917
Al	11.160769	0.012075	7.213876
Al	11.080856	2.852386	7.216247
Al	0.143442	1.398466	6.957767
Al	3.032246	0.000017	7.161427
Al	3.017783	2.836579	7.156613
Al	7.950618	1.385885	7.186768
Al	5.925584	4.250208	7.201001
Al	14.283757	4.462544	7.333825

O	7.021710	1.433982	0.033877
O	15.013184	1.439779	0.042242
O	7.057964	4.248815	0.200364
O	15.049438	4.254582	0.208698
O	2.615760	4.238931	0.341588
O	10.607234	4.244718	0.349963
O	2.824696	1.419565	0.398233
O	10.816160	1.425362	0.406598
O	9.030610	2.821299	1.531398
O	1.039156	2.815512	1.523023
O	9.050538	0.010988	1.522086
O	1.059075	0.005201	1.513742
O	12.851236	0.066302	1.660547
O	4.859783	0.060495	1.652193
O	12.834870	2.787367	1.672222
O	4.843407	2.781590	1.663868
O	3.053996	4.226423	2.889659
O	11.013857	4.231956	2.871520
O	3.103270	1.408157	2.956452
O	11.087255	1.413633	2.954507
O	6.991066	1.412820	3.036923
O	14.930639	1.421521	3.015003
O	14.741227	4.238446	3.090231
O	6.823809	4.232616	3.104863
O	5.114048	2.695535	4.391347
O	0.881409	2.816650	4.465731
O	0.901922	0.035345	4.469768
O	5.126855	0.117861	4.384882
O	13.072280	0.132402	4.385138
O	13.065681	2.747902	4.492118
O	8.902339	2.813289	4.551076
O	8.929113	0.054066	4.567804
O	10.970785	4.231010	5.858370
O	14.894405	1.426165	5.664877

O	15.075861	4.265022	5.689075
O	11.116453	1.454255	5.912923
O	2.974550	4.226429	5.793754
O	7.119869	4.243755	5.756736
O	3.097763	1.423358	5.860305
O	6.931654	1.417242	5.723922
O	1.131833	2.877988	6.945004
O	1.177840	-0.041303	6.926362
O	4.883564	0.021644	7.034560
O	4.884136	2.819815	7.042353
O	9.137031	2.882546	7.208361
O	9.200869	-0.034625	7.234885
O	12.978909	0.059434	7.114991
O	13.045514	2.869291	7.322123
Pt	2.542321	1.419220	9.356824
Pt	2.581379	4.244657	9.282067
Pt	7.080362	4.345270	9.337439
Pt	7.045588	1.409187	9.379187
Pt	0.099193	2.842546	9.024771
Pt	-0.042795	-0.089808	9.010919
Pt	4.816885	2.838269	9.881182
Pt	4.799452	0.036057	9.991909
Pt	2.248502	2.751255	12.018150
Pt	2.302415	0.051515	11.965730
Pt	-0.066453	4.194831	11.372870
Pt	0.110130	1.376834	11.259900
Pt	4.571745	4.244351	12.397050
Pt	4.602008	1.436264	12.448200
H	8.754501	3.324327	8.048816
H	8.779993	-0.433640	8.100286
H	1.658859	4.212948	11.159230
H	11.090408	1.472330	8.324542
H	13.350217	2.324943	8.089771
H	11.052073	4.243095	8.310661

H	3.359426	0.600979	13.265540
H	4.643363	2.880373	13.507310
H	8.015328	2.828901	9.581295
H	5.465651	2.808311	11.513650

Table S3. Calculated atomic charges on H atoms.

H atom	Charge / e
AlO–H (1)	1.00
AlO–H (2)	1.00
AlO–H (3)	1.00
Al–H–Al (4)	−0.95
Al–H–Al (5)	−0.97
terrace Pt–H–Pt (6)	−0.04
edge Pt–H–Pt (7)	−0.08
perimeter Pt–H–Pt (8)	−0.15
Pt_3–H_{fcc} (9)	−0.06
Pt_3–H_{hcp} (10)	−0.07

Table S4. Calculated frequencies and description of vibrational modes that dominantly come from the motion of H atoms.

#Mode[a]	Description	H atoms[b]	Frequency / meV
1	AlO–H stretching	AlO–H (1)	433.7
2	AlO–H stretching	AlO–H (3)	345.6
3	AlO–H stretching	AlO–H (2)	305.8
4	Pt–H stretching	edge Pt–H–Pt (7)	175.9
5	Al–H stretching	Al–H–Al (4, 5)	174.4
6	Pt–H stretching	terrace Pt–H–Pt (6)	170.2
7	Pt–H stretching	perimeter Pt–H–Pt (8)	166.0
8	Al–H stretching	Al–H–Al (4, 5)	163.9
9	Al–H stretching	Al–H–Al (4, 5)	159.9
10	AlO–H bending	AlO–H (2, 3)	144.3
11	Pt–H stretching	Pt_3–H_{hcp} (10)	136.5
12	Pt–H stretching	Pt_3–H_{fcc} (9)	133.1
13	Pt–H stretching	perimeter Pt–H–Pt (8), Pt_3–H_{fcc} (9)	131.8
14	Pt–H stretching	perimeter Pt–H–Pt (8), Pt_3–H_{fcc} (9)	130.9
15	Al–H stretching	Al–H–Al (4, 5)	130.0
16	AlO–H bending	AlO–H (2, 3)	125.9
17	Pt–H stretching	Pt_3–H_{hcp} (10)	121.2
18	AlO–H bending+Al–H bending	AlO–H (1), Al–H–Al (4, 5)	121.0
19	AlO–H bending+Al–H bending	AlO–H (1), Al–H–Al (4, 5)	115.6
20	AlO–H bending+Al–H bending	AlO–H (1), Al–H–Al (4, 5)	109.4
21	Pt–H stretching	edge Pt–H–Pt (7), Pt_3–H_{fcc} (9)	107.1
22	Pt–H stretching	Pt_3–H_{hcp} (10)	105.3
23	Pt–H stretching	edge Pt–H–Pt (7), Pt_3–H_{fcc} (9)	105.2
24	AlO–H bending	AlO–H (2, 3)	102.8
27	AlO–H bending	AlO–H (2, 3)	94.4
33	AlO–H bending	AlO–H (1)	83.5
36	Pt–H bending	perimeter Pt–H–Pt (8)	79.6
49	Pt–H bending	Pt_3–H_{fcc} (9)	69.0
67	Pt–H bending	edge, terrace Pt–H–Pt (6, 7)	56.4
68	Pt–H bending	edge, terrace Pt–H–Pt (6, 7)	56.1
74	Pt–H bending	edge, terrace Pt–H–Pt (6, 7)	53.0

[a]Numbering of normal modes in descending order of frequency. [b]H atoms relevant to the vibrational mode.