Supplementary Material (ESI) for PCCP

Supplementary Information to:

Mechanistic and Spectroscopic Identification of initial Reaction Intermediates for Prenal Decomposition on a Platinum Model Catalyst

J. Haubrich[a,b*], D. Loffreda [c], F. Delbecq [c], P. Sautet [c], Y. Jugnet [d], A. Krupski [e], C. Becker [a], K. Wandelt [a]

Table 1. Vibrational analysis of the dehydro-η^3-triσ(CCC)-prenal-H1 species on Pt(111) (coverage 1/9 ML). The letters following the computed intensities refer to the relative strength, i.e. (v)w = (very) weak, m = medium and (v)s = (very) strong. The coupling of different vibrations is indicated by (+) (in phase) and (-) (anti-phase movement). The abbreviations fR and fT refer to frozen rotations and translations, respectively.

Number	Normal Mode	ω [cm^{-1}]	Intensity	Rel. Intensity
1	ν(C4-H2)	3042	1.2E-08	
2	ν(C5-H5)	3030	5.3E-09	
3	ν_{as}(C4-H3,4)	3004	1.7E-07	
4	ν(C2-H1)	2958	1.3E-07	
5	ν_{as}(C5-H6,7)	2949	5.7E-07	
6	ν_s(C4H$_3$)	2928	1.8E-07	
7	ν_s(C5H$_3$)	2879	1.5E-08	
8	ν(C1=O)	1718	1.1E-05	s
9	δ_s'(C4H$_3$-C5H$_3$)	1429	6.5E-07	
10	δ_s"(C4H$_3$-C5H$_3$)	1421	7.0E-08	
11	δ_{as}"(C4H$_3$-C5H$_3$)	1403	4.6E-08	
12	δ_{as}'(C4H$_3$-C5H$_3$)	1394	2.4E-07	
13	u_s(C4H$_3$-C5H$_3$)	1351	4.7E-07	
14	u_{as}(C4H$_3$-C5H$_3$)	1332	9.9E-09	
15	δ(C2H1)	1209	1.0E-07	
16	ν(C2=C3)	1160	5.7E-08	
17	ν_{as}(C3C4-C3C5)	1105	1.5E-08	
18	γ_s"(C4H$_3$-C5H$_3$)	1042	3.8E-06	m
19	ν(C1-C2)	972	1.7E-07	
20	γ_{as}'(C4H$_3$-C5H$_3$)	953	9.8E-07	w
21	γ(C2H1)	915	5.6E-07	
22	γ_{as}"(C4H$_3$-C5H$_3$)	907	7.5E-08	
23	γ_s'(C4H$_3$-C5H$_3$)	892	4.2E-08	
24	ν_s(C3C4-C3C5)	763	1.8E-06	m
25	ν_{as}(PtC1-PtC2)	640	4.8E-06	s
26	δ(C1-C2=C3)	552	1.2E-07	
27	ν_s(PtC1-PtC2)-ν(PtC3)	503	4.7E-10	
28	ν_s(PtC1-PtC2)+ν(PtC3)	435	3.5E-06	m
29	δ(C2=C3,4,5)	403	2.3E-07	
30	δ(C3-C4,5)	346	4.7E-07	
31	τ_s(CH$_3$)	283	5.3E-08	
32	τ(C2=C3)	267	1.5E-06	w
33	τ_{as}(CH$_3$)	245	2.6E-07	
34	τ(C1-C2)	229	4.1E-07	
35	ω(C2=C3,4,5)	220	3.6E-07	
36	δ(O=C1-C2)	183	3.0E-07	
37	fT	126	2.1E-09	
38	fT	91	2.9E-07	
39	fR	56	1.1E-08	

Table 2. Vibrational analysis of the η^2-isobutenyl species on Pt(111) (coverage 1/9 ML). The harmonic frequencies ω are given in cm^{-1}.

Number	Normal Mode	ω [cm^{-1}]	Intensity	Rel. Intensity
1	ν_s(C3H2-C4H5)	3033	1.6E-08	
2	ν_{as}(C3H2-C4H5)	3031	5.2E-11	
3	ν_{as}(C3-H3,H4)	2978	2.4E-07	
4	ν_{as}(C4-H6,H7)	2975	1.1E-07	
5	ν(C1-H1)	2949	5.8E-09	
6	$\nu_s(C3H_3)+\nu_s(C4H_3)$	2916	1.6E-07	
7	$\nu_s(C3H_3)-\nu_s(C4H_3)$	2912	6.6E-09	
8	δ_s"($C3H_3$-$C4H_3$)	1424	3.1E-07	
9	δ_s'($C3H_3$-$C4H_3$)	1421	7.9E-08	
10	δ_{as}"($C3H_3$-$C4H_3$)	1403	1.9E-10	
11	δ_{as}'($C3H_3$-$C4H_3$)	1397	4.7E-10	
12	u_s($C3H_3$-$C4H_4$)	1344	1.1E-07	
13	u_{as}($C3H_3$-$C4H_3$)	1324	1.3E-08	
14	ν(C1-C2)	1197	3.2E-08	
15	ν_{as}(C2C3-C2C4)	1106	2.6E-09	
16	δ(C1H1)	1077	7.9E-07	m
17	γ_s"($C3H_3$-$C4H_3$)	1026	2.2E-06	s
18	γ_{as}'($C3H_3$-$C4H_3$)	956	1.1E-08	
19	γ_s'($C3H_3$-$C4H_3$)	931	6.7E-09	
20	γ_{as}"($C3H_3$-$C4H_3$)	901	1.4E-09	
21	ν_s(C2C3-C2C4)	802	8.6E-07	m
22	γ(C1H1)	697	8.9E-09	
23	ν_s(Pt1C1-Pt2C1)-ν(Pt3C2)	592	8.5E-07	m
24	ν_{as}(Pt1C1-Pt2C1)	520	7.4E-09	
25	ν_s(Pt1C1-Pt2C1)+ν(Pt3C2)	456	2.6E-06	s
26	δ(C2-C3-C4)	377	1.9E-09	
27	τ(C1-C2)	280	6.9E-09	
28	δ(C1-C2-C3,C4)	258	2.1E-07	
29	τ_s($C3H_3$)	232	6.8E-08	
30	τ_{as}($C3H_3$)	202	3.0E-07	
31	fR	157	4.0E-08	
32	fT	149	2.1E-07	
33	fR	117	4.1E-09	

[b] From Ref. [1].

Table 3. Vibrational analysis of the η^1-isobutylidyne bonded in a threefold hollow site on Pt(111) (coverage 1/9 ML).

Number	Normal Mode	ω [cm^{-1}]	Intensity	Rel. Intensity	HREELS[a]	HREELS[b]
1	ν_{as}(C3-H2,4)	3041	1.5E-07			
2	ν_{as}(C4-H5,7)	3038	7.3E-08		3017	
3	ν_{as}(C3-H3,4)	3035	1.6E-07		2953	2970 ($\nu_{as}(CH_3)$)
4	ν_{as}(C4-H6,7)	3032	1.4E-08			
5	$\nu_s(C3H_3)$	2963	1.4E-07		2875	2880 ($\nu_s(CH_3)$)
6	$\nu_s(C4H_3)$	2959	3.0E-08			
7	ν(C2-H1)	2929	3.3E-08			
8	δ_s''($C3H_3$-$C4H_3$)	1452	4.8E-07	vw	1452	1460 ($\delta_{as}(CH_3)$)
9	δ_s'($C3H_3$-$C4H_3$)	1440	1.2E-09			
10	δ_{as}''($C3H_3$-$C4H_3$)	1429	7.5E-10			
11	δ_{as}'($C3H_3$-$C4H_3$)	1427	1.3E-09			ca 1400 ($\delta_s(CH_3)$)
12	u_s($C3H_3$-$C4H_3$)	1359	1.1E-08		1367	
13	u_{as}($C3H_3$-$C4H_3$)	1336	1.6E-09		1327	
14	δ(C1H1)	1252	3.4E-08			1280 (δ(CH))
15	γ(C1H1)	1251	3.0E-10			
16	γ_s''($C3H_3$-$C4H_3$)	1149	1.1E-09			
17	ν_{as}(C2-C3,C2-C4)	1070	1.7E-11			
18	γ_s'($C3H_3$-$C4H_3$)	1064	1.5E-07		1028	1080, 1010, 800
19	ν(C1-C2)	965	3.1E-06	s	965	(coupled ν(CC)
20	γ_{as}'($C3H_3$-$C4H_3$)	937	1.1E-09			and $\gamma(CH_3)$)
21	γ_{as}''($C3H_3$-$C4H_3$)	901	3.3E-11			
22	ν_s(C2-C3,C2-C4)	831	7.2E-09		797	
23	ν(Pt1C-Pt2C+Pt3C)	562	3.6E-11		585	645 (ν(CPt),
24	ν(Pt1C+Pt2C-Pt3C)	554	4.5E-09		460	δ(CCC))
25	ν(Pt1C-Pt3C-Pt2C)	418	1.3E-07		405	440 (ν(CPt))
26	δ(C2-C3-C4)	376	4.4E-09			
27	$\tau_s(CH_3)$	251	1.4E-08			
28	δ(C1-C2-C3,C4)	242	5.7E-08			
29	$\tau_{as}(CH_3)$	225	1.6E-08			
30	τ(C1-C2)	220	3.3E-07			
31	fT	125	2.8E-07			
32	fT	104	1.2E-08			
33	fR	54	5.6E-10			

[a] Actual work, 4.9L prenal annealed to 440 K.

[b] From Ref. [1].

Table 4. Vibrational analysis of the η^1-methylidyne bonded in a threefold hollow site on Pt(111) (coverage 1/4 ML).

Number	Normal Mode	ω [cm^{-1}]	Intensity	Rel. Intensity	HREELS[a]	HREELS[b]
1	ν(CH)	3024	2.8E-08	m	2964	2970
2	$\nu_{as}(Pt_3C)$+fT (degenerate)	778	1.3E-08	w	796	800
3	$\nu_{s}(Pt_3C)$	610	0		643	640
4	fT+$\nu_{as}(Pt_3C)$ (degenerate)	473	4.0E-09		465	

[a] Actual work, 4.9L prenal annealed to 440 K.

[b] From Ref. [1].

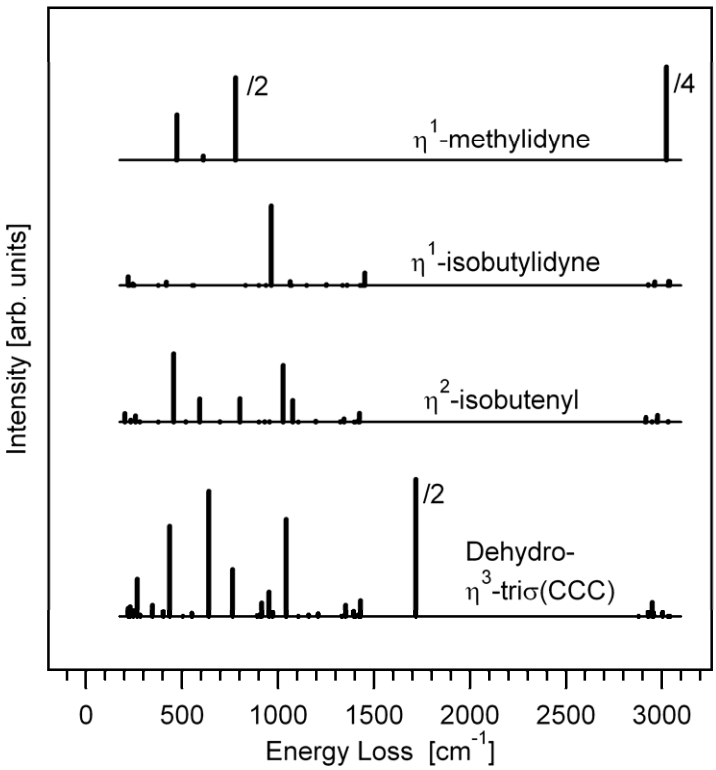

Figure 1. Comparison of the computed HREEL spectra of the four identified surface intermediates during prenal decomposition on Pt(111). See the Computational Details Section of a description of the theoretical vibrational simulations.

Notes and references

[a] *Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany, Fax: +49-228-73-2515; Tel: +49-228-73-2253; E-mail: janh@pc.uni-bonn.de*
[b] *Dept. of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA*
[c] *Université de Lyon, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon and CNRS, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France*
[d] *Institut de Recherche sur la Catalyse et l'Environnement de Lyon UMR5256 CNRS-Université Lyon 1, 2 avenue A. Einstein, F-69626 Villeurbanne, France*
[e] *Institute of Experimental Physics, University of Wrocław, pl. Maxa Borna 9, PL 50-204 Wrocław, Poland*

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