

# The influence of charge on the reactivity of supported heterogeneous transition metal catalysts

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## Support Information

Table S1. The loss of Hirshfeld charges of Pt clusters vs H coverage

	m=2	m=4	m=6	m=8	m=10	m=12	m=14	m=16	m=18
Pt <sub>4</sub> <sup>+</sup> H <sub>m</sub>	-0.046	-0.104	-0.131	-0.026					
Pt <sub>4</sub> H <sub>m</sub>	-0.151	-0.236	-0.333	-0.381	-0.425	-0.521	-0.574	-0.626	
Pt <sub>4</sub> <sup>-</sup> H <sub>m</sub>	-0.247	-0.475	-0.634	-0.832	-0.940	-1.072	-1.219	-1.333	-1.468

Table S2: The number of H atoms for different Pt cluster sizes and charge states at full saturation.

	n=2	n=4	n=6	n=8
Pt <sub>n</sub> <sup>+</sup> H <sub>m</sub>	6	8	18	30
Pt <sub>n</sub> H <sub>m</sub>	8	16	24	32
Pt <sub>n</sub> <sup>-</sup> H <sub>m</sub>	10	18	26	34

Table S3: Energies for hydrogenation of ethylene on H-saturated Pt clusters.

	Activation energy (kcal/mol)			Reaction energy (kcal/mol)		
	Cationic	neutral	anionic	cationic	neutral	anionic
Pt <sub>2</sub>	14.35	28.21	22.85	-43.74	-24.07	-41.94
Pt <sub>4</sub>	14.57	18.23	24.63	-26.77	-9.01	-32.74
Pt <sub>6</sub>	11.97	12.91	19.00	-36.37	-23.15	-23.83
Pt <sub>8</sub>	10.52	12.52	20.27	-17.18	-25.55	-19.75

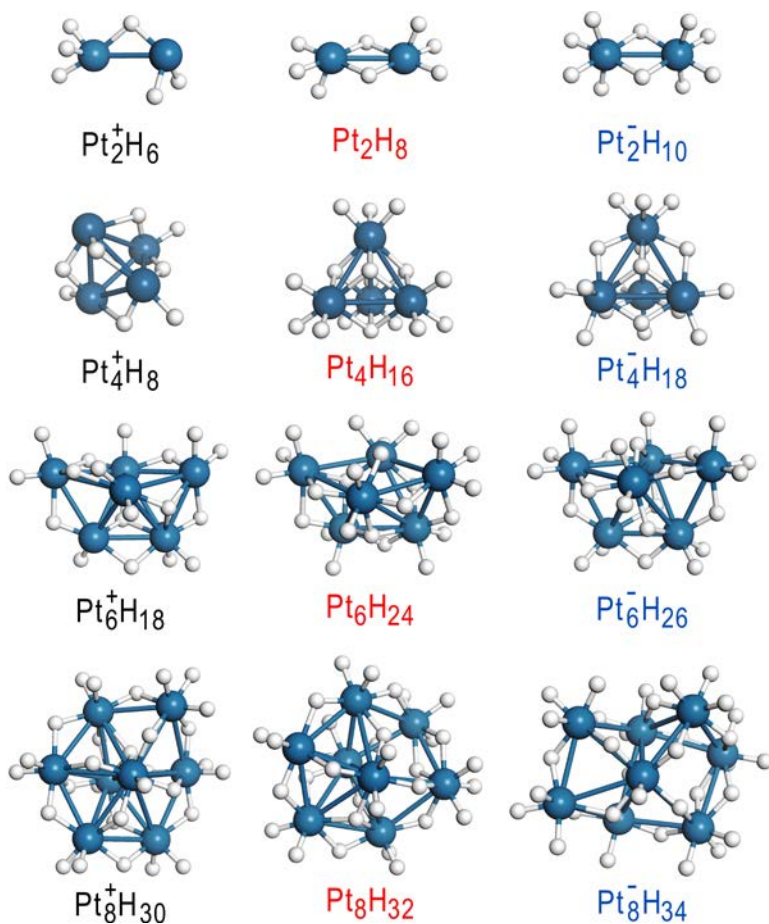


Figure S1: Structures of full H saturated hydrides

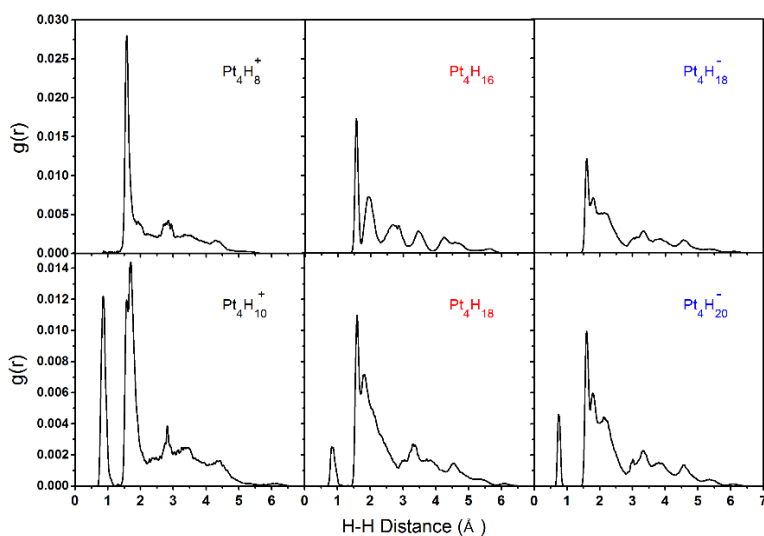


Figure S2. Calculated H-H distance distribution function  $g(r)$  of full H saturated structures at 423 K. The saturation limits are identical to those found at room temperature (see Figure 4).

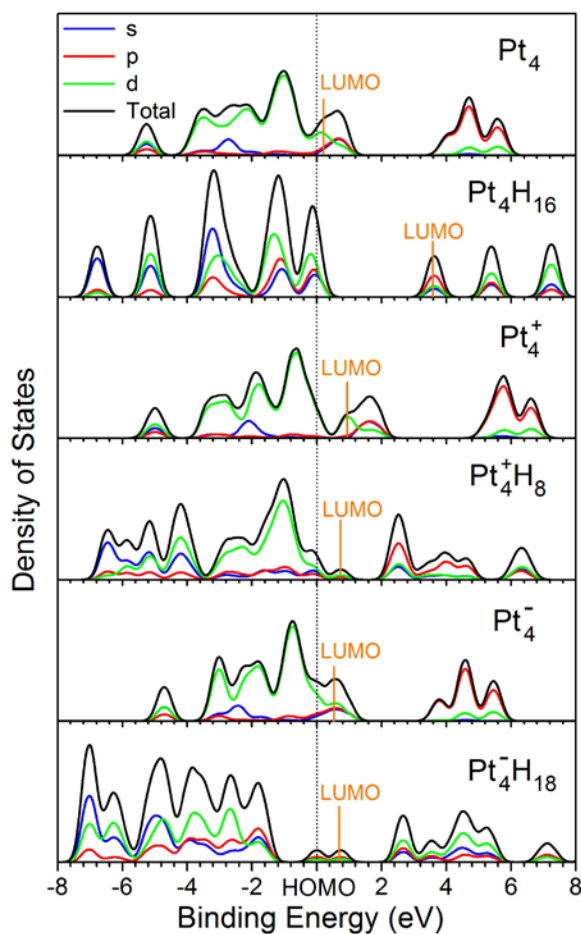


Figure S3. The calculated density of states of the bare Pt clusters and the fully H saturated clusters. Detailed analysis indicates that the orbital overlaps between the 1s orbital of H atoms and the 5d orbitals of Pt atoms occur when the fully H saturated clusters ( $\text{Pt}_4^+\text{H}_8$ ,  $\text{Pt}_4\text{H}_{16}$ , and  $\text{Pt}_4^-\text{H}_{18}$ ) are formed, which is consistent with the calculated charge transfer from Pt clusters to H atoms.