A systematic study on Pt based, subnanometer-sized alloy cluster catalysts for alkane dehydrogenation: Effects of intermetallic interaction

Andreas W. Hauser,[*,†,¶] Paul R. Horn,[‡] Martin Head-Gordon,[‡] and Alexis T. Bell[*,†]

†*Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462*

‡*Department of Chemistry, University of California, Berkeley, CA 94720-1462*

¶*Current address: Graz University of Technology, Institute of Experimental Physics, Petersgasse 16, 8010 Graz, Austria*

E-mail: andreas.w.hauser@gmail.com; alexbell@uclink.berkeley.edu

Sections 1 and 2 of this Supporting Material contain a study on the effects of dispersion correction on the DFT results presented in the main article. Section 3 compares the electronic energies for the second C-H cleavage on all catalysts, a detail we skipped in the main article. In Section 4 we provide information on molecular structures for all systems and configurations under investigation.

Contents

1 Single point B3LYP-D3 calculations on Pt_4

Single point energy calculations, with the D3 correction of Grimme[1] added to the B3LYP functional, were performed for all systems and geometries discussed in the main article. The results are summarized in a series of Figures equivalent to Figures 2-5 of the main article.

Although the inclusion of a van der Waals correction is enhancing the adsorption considerably when compared to the uncorrected B3LYP results (approx. 5 kcal/mol on average), it has no effect on the activity ranking of the catalysts with respect to the barrier height of the rate determining first C-H cleavage step. In general, all trends are the same as in the main article and lead to the same conclusions.

Note, however, that the inclusion of a van der Waals correction does affect the absolute barrier heights, leading to higher activities but reduced selectivities. A stronger binding of the reactant reduces the barrier for the rate determining step, but also the barrier for the undesired additional dehydrogenation step after the second C-H bond cleavage.

1.1 D3-corrected reaction pathways for C_3H_8@Pt_4

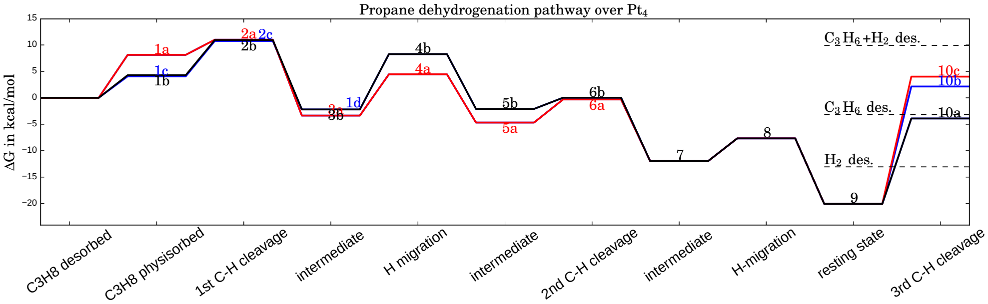

Figure 1: Gibbs free energy diagram of possible dehydrogenation pathways, calculated at 400 ° C (single point B3LYP-D3 values at B3LYP-converged geometries) The first hydrogen abstraction is the rate-determining step and is most likely to happen at C1, corresponding to geometry **2b** in Figure 1 of the main article. Desorption energies are plotted as dashed lines. See Table 1 for details.

Table 1: D3-corrected electronic and Gibbs energies for the dehydrogenation of propane over Pt_4 (see Figure 1).

Reaction step	Label	ΔE^a (kcal/mol)	ΔG^a (kcal/mol)
propane adsorption at C2	1a	-17.13	8.13
1^{st} C-H cleavage (TS)	2a	-11.14	10.99
intermediate	3a	-27.12	-3.36
H migration (TS)	4a	-17.64	4.45
intermediate	5a	-26.16	-4.68
2^{nd} C-H cleavage at C1 (TS)	6a	-23.49	-0.31
propane adsorption at C1, convex	1b	-16.65	4.29
1^{st} C-H cleavage (TS)	2b	-10.81	10.93
intermediate	3b	-25.63	-2.20
H migration (TS)	4b	-15.14	8.27
intermediate	5b	-24.07	-2.10
2^{nd} C-H cleavage at C2 (TS)	6b	-23.01	0.02
2^{nd} C-H cleavage at C1 (TS)		-4.28	16.34
propane adsorption at C1, concave	1c	-17.14	4.07
1^{st} C-H cleavage (TS)	2c	-11.61	10.75
propane adsorption, symmetric	1d	-18.04	2.91
intermediate	7	-34.54	-11.96
H migration (TS)	8	-29.71	-7.68
intermediate	9	-44.43	-20.07
3^{rd} C-H cleavage at C3 (TS)	10a	-23.13	-3.91
3^{rd} C-H cleavage at C2 (TS)	10b	-14.55	2.14
3^{rd} C-H cleavage at C1 (TS)	10c	-15.37	4.01
hydrogen desorption from Pt_4-C_3H_6		-13.36	-13.06
propene desorption from Pt_4-H-H		2.74	-3.15
hydrogen and propene desorption[b]		36.81	9.92
C-C breaking in Pt_4-C_3H_8		8.45	32.43
C-C breaking in H-Pt_4-CH_3-CH-CH_3		10.62	31.65
C-C breaking in H-Pt_4-CH_3-CH_2-CH_2		5.37	27.94
C=C breaking in H-H-Pt_4-C_3H_6		26.34	41.48

[a] Relative to the energy of a pure Pt_4 cluster and a propane molecule at infinite distance.

[b] These values correspond to the electronic and Gibbs free energies for the gas phase reaction $C_3H_8 \rightleftharpoons C_3H_6 + H_2$.

2 Single point B3LYP-D3 calculations on Pt$_3X$

2.1 Electronic energies for the adsorption of propane onto Pt$_3X$

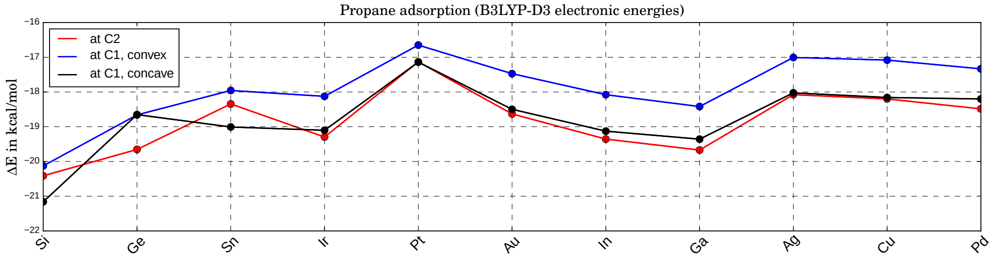

Figure 2: Electronic energies for the adsorption of propane onto Pt$_3X$ (see **1a**, **1b** and **1c** in Figure 1 of the main article) at zero Kelvin. Due to the still weak adsorption (despite the D3 correction) the Gibbs free energies are all positive at experimentally relevant temperatures, indicating a negligible coverage of the catalyst with physisorbed propane.

2.2 Comparison of energy barriers for the first TS states of Pt$_3X$

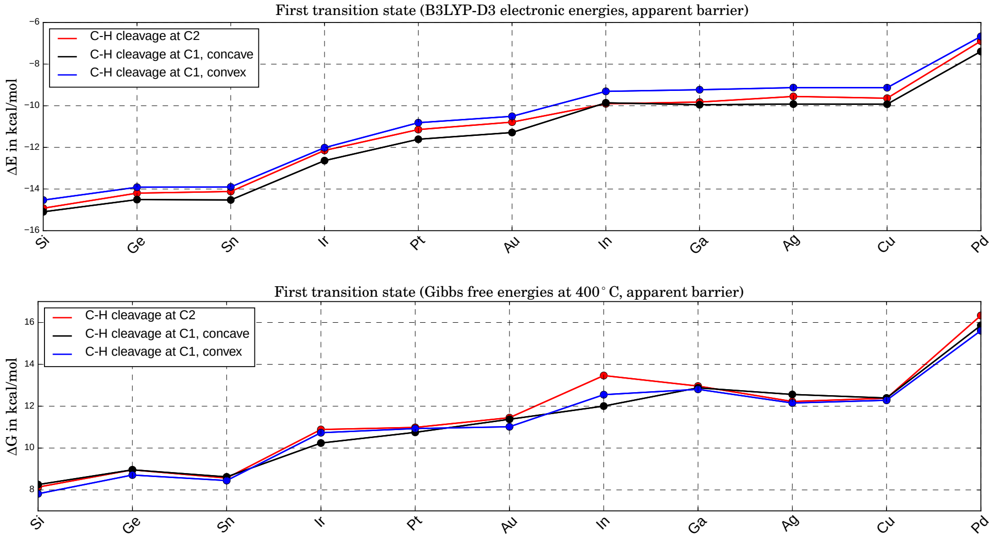

Figure 3: Comparison of electronic energy barriers (upper graph) and apparent Gibbs free energy barriers at 400° (lower graph) for the first TS states of Pt$_3X$ (see **2a**, **2b** and **2c** in Figure 1 of the main article). For all alloys the lowest of these options for the first C-H bond cleavage corresponds to the rate-determining step. The ranking with respect to electronic energy barrier height is the same as obtained with uncorrected B3LYP.

2.3 Comparison of ΔG values for propene desorption and alternative reaction pathways

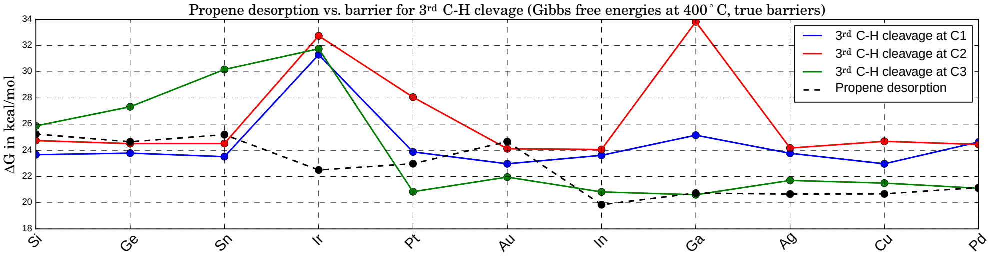

Figure 4: Comparison of ΔG values for propene desorption and for the true barrier that has to be overcome for continued C-H bond breaking at 400°. The difference between the lowest solid line (bond cleavage) and the dashed line (desorption) can be interpreted as a descriptor for the catalyst selectivity towards propene.

3 B3LYP and B3LYP-3D energy barriers for the second C-H cleavage on Pt_3X

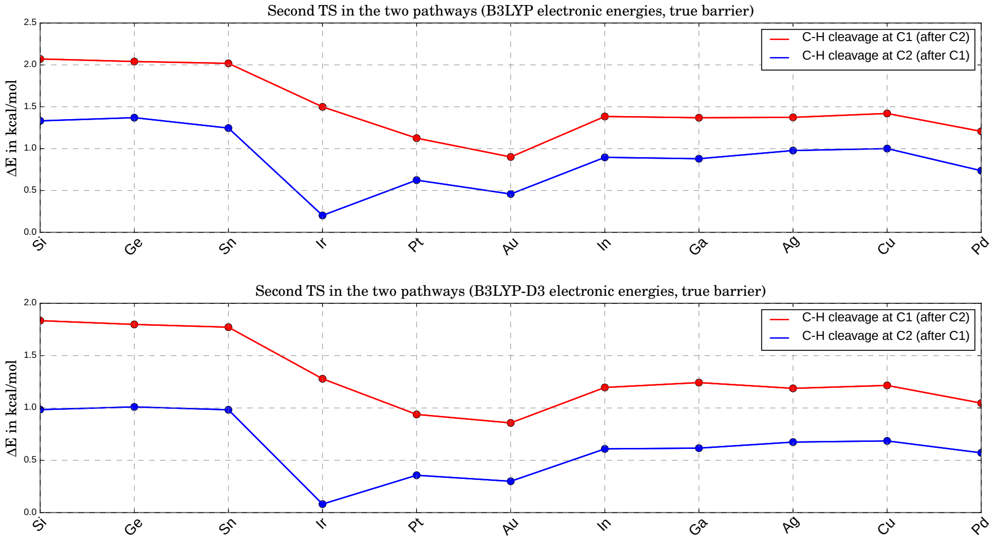

Figure 5: B3LYP (upper graph) and B3LYP-3D (lower graph) electronic energies for the second C-H bond cleavage in the propane dehydrogenation pathway on Pt_3X. Differences in barrier heights for different alloys are minimal. The corresponding geometries are similar to steps **5a/6a** and **5b/6b** in Figure 1 of the main article, but without the remaining H atom from the previous dehydrogenation step.

4 B3LYP geometries for all systems and configurations

All geometries are written into separate txt files and zipped into a single archive for convenience. The format is xyz; charge and multiplicity are also provided for each geometry.

References

(1) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *The Journal of Chemical Physics* **2010**, *132*.