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## Correction: A quantum chemical study of hydrogen adsorption on carbon-supported palladium clusters

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Correction for 'A quantum chemical study of hydrogen adsorption on carbon-supported palladium clusters' by Lisa Warczinski et al., *Phys. Chem. Chem. Phys.*, 2019, 21, 21577–21587, DOI: 10.1039/c9cp04606b.

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We correct an error to our previous paper,<sup>1</sup> which does not affect the key statements of the paper but changes some values and one minor conclusion. In our previous paper, the calculation of the Gibbs free enthalpies was missing electronic contributions and an incorrect scaling parameter for the vibrational frequencies was used. Here, we report the corrected values for the Gibbs free enthalpies including all necessary contributions and employing the correct vibrational frequency scaling parameter of 1.0190 for the def2-SVP basis set and the TPSS functional.<sup>2</sup>

The first values we need to correct are the Gibbs free enthalpies of adsorption of several hydrogen molecules on Pd<sub>6</sub>. The corrected values are shown in the reproduced Tables 2 and 3. All the corresponding conclusions are still valid.

**Table 2** Incremental adsorption energies  $\Delta E_{\text{ads}}$  and Gibbs free enthalpies  $\Delta G_{\text{ads}}$  in kJ mol<sup>−1</sup> for an increasing number of H<sub>2</sub> molecules on free Pd<sub>6</sub>

Number of H <sub>2</sub>	$\Delta E_{\text{ads}}$	$\Delta G_{\text{ads}}$
1	−49.2	−24.8
2	−43.8	−9.7
3	−43.7	−20.1
4	−37.8	−10.0
5	−33.7	−9.4
6	−24.2	+6.8
7	−64.8	−22.5

**Table 3** Incremental adsorption energies  $\Delta E_{\text{ads}}$  and Gibbs free enthalpies  $\Delta G_{\text{ads}}$  in kJ mol<sup>−1</sup> for an increasing number of H<sub>2</sub> molecules on carbon-supported Pd<sub>6</sub>

Number of H <sub>2</sub>	$\Delta E_{\text{ads}}$	$\Delta G_{\text{ads}}$
1	−56.2	−28.5
2	−33.3	−3.2
3	−33.6	−12.0
4	−66.8	−27.7
4s	−30.5	+9.7

In contrast to that, the free activation enthalpies for the hydrogen dissociation on Pd<sub>6</sub> changed noticeably:

- free Pd<sub>6</sub>: 40.4 kJ mol<sup>−1</sup> (old: 1.4 kJ mol<sup>−1</sup>)
- carbon-supported *cis*-configuration: 45.2 kJ mol<sup>−1</sup> (old: 3.3 kJ mol<sup>−1</sup>)
- carbon-supported perpendicular configuration: 22.2 kJ mol<sup>−1</sup> (old: 4.1 kJ mol<sup>−1</sup>)

Therefore, we have to correct our conclusion that hydrogen dissociation on free Pd<sub>6</sub> should occur spontaneously at room temperature.  $\Delta G^\ddagger$  is, at 40.4 kJ mol<sup>−1</sup>, rather high for this. However, this further confirms our result that it is essential to also study larger cluster sizes (*vide infra*). Additionally, the conclusion that hydrogen dissociation on carbon-supported Pd<sub>6</sub> should occur



**Table 4** Incremental dissociation energies  $\Delta E_{\text{diss}}$  and Gibbs free enthalpies  $\Delta G_{\text{diss}}$  in  $\text{kJ mol}^{-1}$  for an increasing number of  $\text{H}_2$  molecules on free  $\text{Pd}_6$ 

Number of $\text{H}_2$	$\Delta E_{\text{diss}}$	$\Delta G_{\text{diss}}$
1	−66.7	−36.3
2	−45.7	−15.7
3	−71.5	−42.7
4	−68.8	−32.4

**Table 5** Incremental dissociation energies  $\Delta E_{\text{diss}}$  and Gibbs free enthalpies  $\Delta G_{\text{diss}}$  in  $\text{kJ mol}^{-1}$  for an increasing number of  $\text{H}_2$  molecules on carbon-supported  $\text{Pd}_6$ 

Number of $\text{H}_2$	$\Delta E_{\text{diss}}$	$\Delta G_{\text{diss}}$
1	−100.0	−72.1
2	−62.8	−33.1
3	−106.1	−71.9

spontaneously at room temperature is still valid. The free activation barrier for the dissociation is smaller than the Gibbs free enthalpy change for the initial molecular adsorption step.

Also, the values for the Gibbs free enthalpies of dissociation of several hydrogen molecules on  $\text{Pd}_6$  are affected. However, all the corresponding conclusions are still valid. Tables 4 and 5 are reproduced here and list the corrected values. Further changes are:

- The third hydrogen molecule has a free dissociation enthalpy  $36.7 \text{ kJ mol}^{-1}$  more favourable for the carbon-supported system compared to the free system (old:  $18.8 \text{ kJ mol}^{-1}$ ).
- If one adds one hydrogen atom of the second hydrogen molecule not to the top, but to the unfavourable lower layer of the cluster, the cluster deforms and shows a favourable free dissociation enthalpy of  $-48.3 \text{ kJ mol}^{-1}$  (old:  $-18.8 \text{ kJ mol}^{-1}$ ).

Also, the changes for the  $\text{Pd}_{21}$  systems are negligible and all conclusions drawn previously are still valid. The following list reports the changes which occurred due to the correction of the mistake for the  $\text{Pd}_{21}$  systems:

- Free activation enthalpy for the hydrogen dissociation on free  $\text{Pd}_{21}$ :  $13.8 \text{ kJ mol}^{-1}$  (old:  $2.7 \text{ kJ mol}^{-1}$ )
- Free activation enthalpy for the H atom migration from the red configuration:  $6.6 \text{ kJ mol}^{-1}$  (old:  $10.5 \text{ kJ mol}^{-1}$ )
- Free activation enthalpy for the H atom migration from the yellow configuration:  $5.0 \text{ kJ mol}^{-1}$  (old:  $6.3 \text{ kJ mol}^{-1}$ )

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

## References

- 1 L. Warczinski and C. Hättig, *Phys. Chem. Chem. Phys.*, 2019, **21**, 21577–21587.
- 2 M. K. Kesharwani, B. Brauer and J. M. L. Martin, *J. Phys. Chem. A*, 2015, **119**, 1701–1714.

