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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,¹ 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.²

The first values we need to correct are the Gibbs free enthalpies of adsorption of several hydrogen molecules on Pd₆. The corrected values are shown in the reproduced Tables 2 and 3. All the corresponding conclusions are still valid.

Table 2 Incremental adsorption energies ΔE_{ads} and Gibbs free enthalpies ΔG_{ads} in kJ mol^{−1} for an increasing number of H₂ molecules on free Pd₆

| Number of H ₂ | ΔE_{ads} | ΔG_{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 ΔE_{ads} and Gibbs free enthalpies ΔG_{ads} in kJ mol^{−1} for an increasing number of H₂ molecules on carbon-supported Pd₆

| Number of H ₂ | ΔE_{ads} | ΔG_{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 Pd₆ changed noticeably:

- free Pd₆: 40.4 kJ mol^{−1} (old: 1.4 kJ mol^{−1})
- carbon-supported *cis*-configuration: 45.2 kJ mol^{−1} (old: 3.3 kJ mol^{−1})
- carbon-supported perpendicular configuration: 22.2 kJ mol^{−1} (old: 4.1 kJ mol^{−1})

Therefore, we have to correct our conclusion that hydrogen dissociation on free Pd₆ should occur spontaneously at room temperature. ΔG^\ddagger is, at 40.4 kJ mol^{−1}, 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 Pd₆ should occur



Table 4 Incremental dissociation energies ΔE_{diss} and Gibbs free enthalpies ΔG_{diss} in kJ mol^{-1} for an increasing number of H_2 molecules on free Pd_6

| Number of H_2 | ΔE_{diss} | ΔG_{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 ΔE_{diss} and Gibbs free enthalpies ΔG_{diss} in kJ mol^{-1} for an increasing number of H_2 molecules on carbon-supported Pd_6

| Number of H_2 | ΔE_{diss} | ΔG_{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 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 kJ mol^{-1} more favourable for the carbon-supported system compared to the free system (old: 18.8 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 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 Pd_{21} systems:

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

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

References

- 1 L. Warczynski 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.

