Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.




# Supplementary information

## Spot the difference: hydrogen adsorption and dissociation on unsupported platinum and platinum-coated transition metal carbides

**Andrey A. Koverga[a*], Elizabeth Flórez[a], Carlos Jimenez-Orozco[a*], José A. Rodriguez[b]**

[a]Grupo de Investigación Mat&mpac, Facultad de Ciencias Básicas, Universidad de Medellín, Medellín 050026, Colombia.

[b]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, United States

Corresponding authors:

E-mail addresses: akoverga@unal.edu.co (A. Koverga), cjimenez@udem.edu.co (C. Jimenez-Orozco)

# S1. Translational and rotatory partition functions for $H_2$ in the gas phase.

The dependency on temperature (T) of the elementary reaction rate for the dissociation process of molecular hydrogen on the studied surfaces (r) can be estimated using harmonic transition state theory, including translational and rotational partition functions in addition to the vibrational partition function:

$$r = \frac{k_B T}{h} \frac{q_{vib}^{TS}}{q_{vib}^{IS} \cdot q_{tr}^{IS} \cdot q_{rot}^{IS}} e^{-\frac{E_a}{k_B T}} \qquad \text{(S1)}.$$

Here $k_B$ is the Boltzmann constant, $T$ – temperature, $h$ – Plank constant, $Ea$ – activation energy including ZPE contributions, $q^{TS}_{vib}$ and $q^{IS}_{vib}$ – the vibrational partition functions of the TS and IS, respectively and $q^{IS}_{tr}$ and $q^{IS}_{rot}$ are translational and rotational partition functions for the IS. The $q_{vib}$ term is explained in detail in the manuscript, while $q^{IS}_{tr}$ $q^{IS}_{rot}$ can be written as:

$$q_{tr} = \left( \frac{2\pi m_{H_2} k_B T}{h^2} \right)^{3/2} \frac{k_B T}{p_{H_2}} \qquad \text{(S2)},$$

$$q_{rot} = \frac{1}{\sigma_r} \left( \frac{T}{\Theta_r} \right) \text{(S3)},$$

where $m_{H_2}$ is hydrogen molecule mass; for $H_2$ the symmetry number, $\sigma_r = 2$, while $\Theta_r = \frac{h^2}{8\pi I k_B}$, where $I$ is the moment of inertia.

The dissociation rates at surface coverage $\Theta_H$=1/2 ML and T=298 K on all the studied surfaces, calculated using Eqs. 5 and S1 are summarized in Table S1 below:

**Table S1.** $H_2$ dissociation rates at $\Theta_H$=1/2 ML, calculated for all the studied system at 298 K, using equations 5 and S1.

| System | Rate without $q_{rot}$ and $q_{tr}$ | Rate with $q_{rot}$ and $q_{tr}$ |
|---|---|---|
| Pt(111) | $1.94\times10^{11}$ | $8.15\times10^{10}$ |
| Pt/C-$Mo_2C$ | $4.36\times10^{6}$ | $1.83\times10^{6}$ |
| Pt/Mo-$Mo_2C$ | $1.10\times10^{11}$ | $4.60\times10^{10}$ |
| Pt/C-WC | $2.61\times10^{10}$ | $1.10\times10^{10}$ |
| Pt/W-WC | $3.94\times10^{8}$ | $1.65\times10^{8}$ |

From these data, it becomes evident that the impact of including the rotation and translation partition functions does not affect significantly the final values of the reaction rates and, importantly, the tendencies observed for the reaction rate with and without these partition functions are the same. Therefore, throughout this work only the vibrational partition function was used to study the impact of the temperature on the rate of hydrogen dissociation on Pt(111) and Pt/TMC surfaces.

## S2. $H_2$ adsorption characteristics on Pt/TMC and impact of coverage on the geometry of the surface

**Table S2**. Adsorption energies for $H_2$ on Pt/α-WC(0001) and Pt/β-$Mo_2C$ surfaces at all $\Theta_H$ with ΔZPE contribution together with $H_2$—Pt and H—H distances. The activation barrier for the $H_2$formation reaction ($E_{a,rev}$) from adsorbed H* atoms is included as well.

| Surface | Coverage, $\Theta_H$ | d (H—H) / Å | d (Pt—$H_2$) / Å | $E_{ads,H2}$ /eV | $E_{a,rev}$ / eV |
|---|---|---|---|---|---|
| Pt/C-$Mo_2C$ | 1/8 | 0.86 | 1.82 | -0.35 | 0.63 |
| | 1/2 | 0.75 | 3.13 | -0.36 | 2.70 |
| | 1 | 0.75 | 3.29 | -0.29 | 0.38 |
| Pt/Mo-$Mo_2C$ | 1/8 | 0.86 | 1.82 | -0.56 | 0.42 |
| | 1/2 | 0.84 | 1.84 | -0.64 | 0.26 |
| | 1 | 0.78 | 1.75 | -0.67 | 0.22 |
| Pt/C-WC | 1/8 | 0.90 | 1.72 | -0.98 | 0.36 |
| | 1/2 | 0.76 | 3.19 | -0.60 | 0.77 |
| | 1 | 0.76 | 3.15 | -0.41 | 0.34 |
| Pt/W-WC | 1/8 | 0.88 | 1.78 | -0.90 | 0.53 |
| | 1/2 | 0.76 | 1.85 | -0.80 | 0.21 |
| | 1 | 0.76 | 1.86 | -0.68 | 0.04 |
| Pt (111) | 1/2 | 0.75 | 3.43 | -0.32 | 0.92 |
| | 1 | 0.76 | 2.64 | -0.47 | 0.90 |

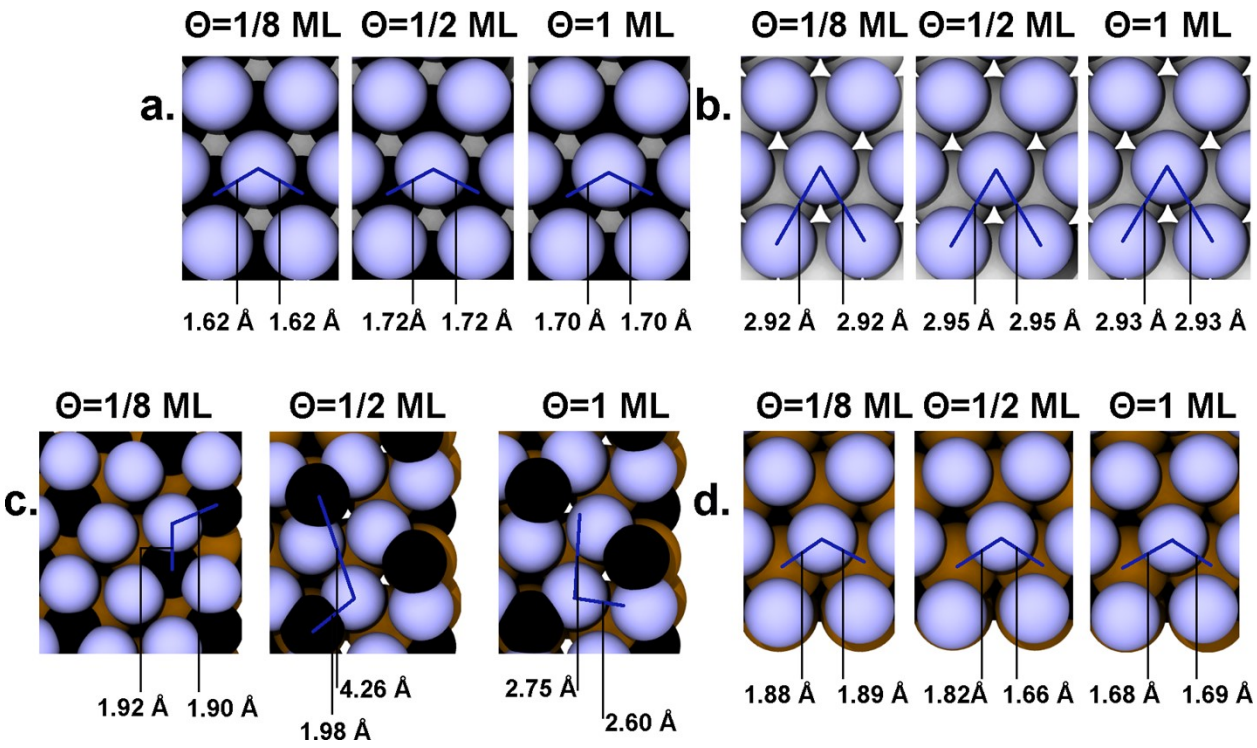


**Fig. S1**. Distances between stable adsorption sites for $H_2$ and atomic H at different surface coverages for: a. Pt/C-WC; b. Pt/W-WC; c. Pt/C-$Mo_2C$ and d. Pt/Mo-$Mo_2C$. The free end of each blue line corresponds to stable adsorption location of a hydrogen atom; the intercrossing of a pair of blue lines is located at the stable adsorption site for $H_2$. While atomic H are not shown on the schematics, their presence is implied at Θ=1/2 and 1 ML.

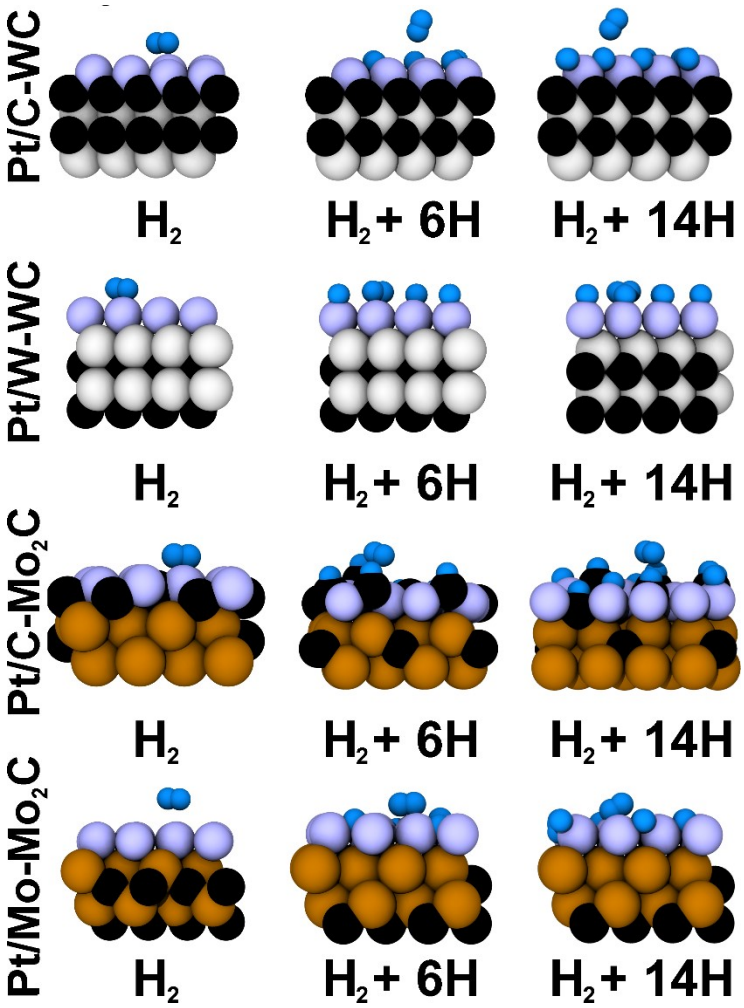


**Fig. S2.** Side views of stable geometries for $H_2$ on Pt/TMC surfaces.