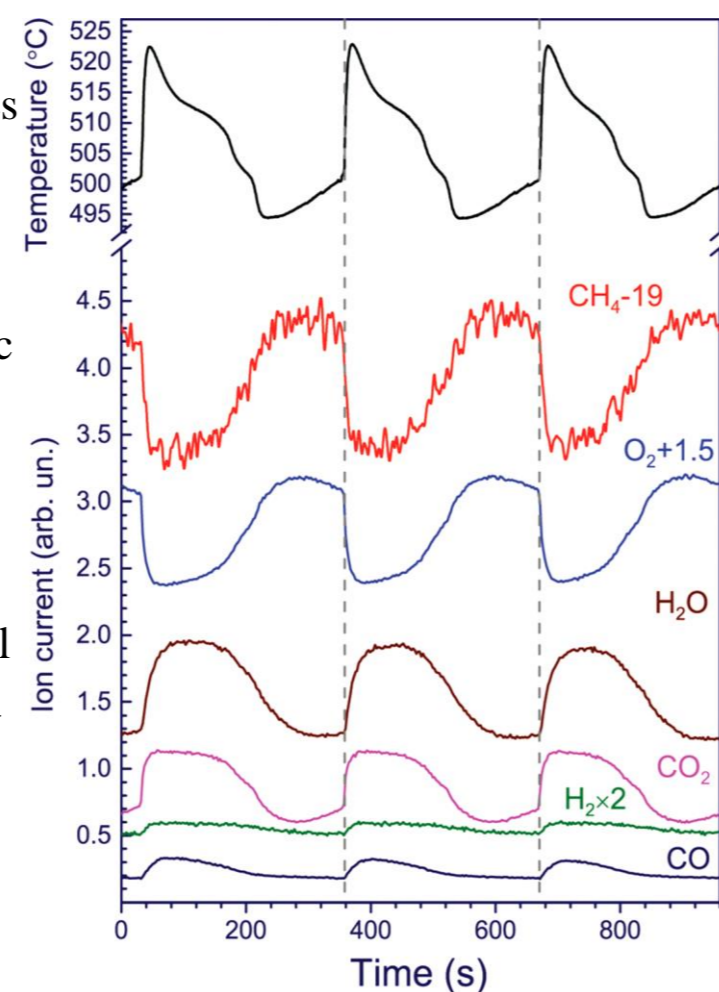


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## Motivations

- ❖ Pd is an important catalyst metal for a wide variety of chemical processes. It is now well established that light element impurities can modify the catalytic performance of Pd. The positive influence of dissolved carbon was shown for selective hydrogenation of alkynes to alkenes.
- ❖ The accumulation of carbon at highly active surface of metallic Pd and its subsequent dissolution in the bulk of the catalyst occurs during the rate oscillations of the methane oxidation under oxygen-deficient conditions [1].
- ❖ Structural transformations of Pd in the oscillation cycle went through fast reduction of Pd oxide, metal carbonization, removal of deposited carbon as CO<sub>2</sub> and gradual oxidation of metallic Pd [2].
- ❖ Pd bulk is simply a storage reservoir for C? Or is palladium carbide the most active phase?



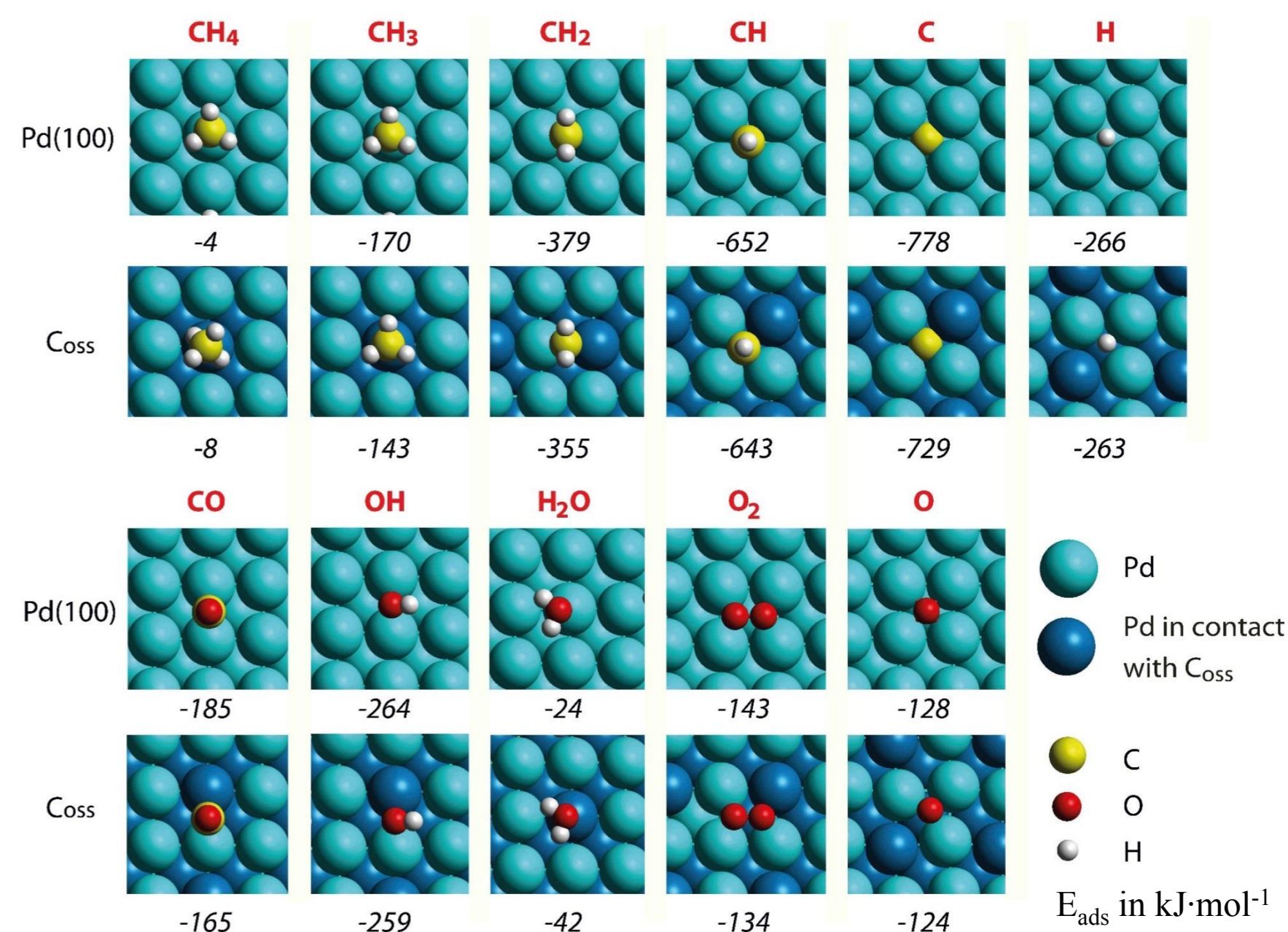
Typical self-sustained oscillations observed in the oxidation of methane on palladium [1].

[1] V. V. Kaichev et al. *Catal. Sci. & Technol.* 2021, 11, 4392.  
 [2] V. Y. Bychkov et al. *Appl. Catal. A: Gen.* 2016, 522, 40.

## Aims

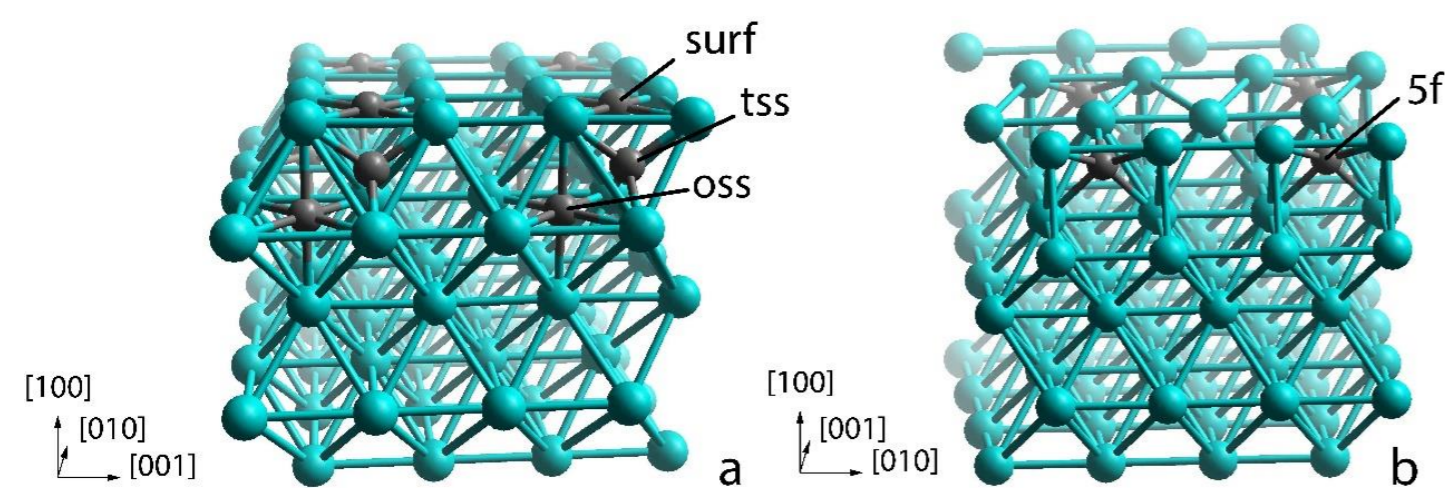
- ❖ To study the effect of dissolved carbon on the reaction mechanism of methane oxidation on palladium using theoretical calculations.

## Influence of subsurface carbon On the adsorption of intermediates



## Method and model

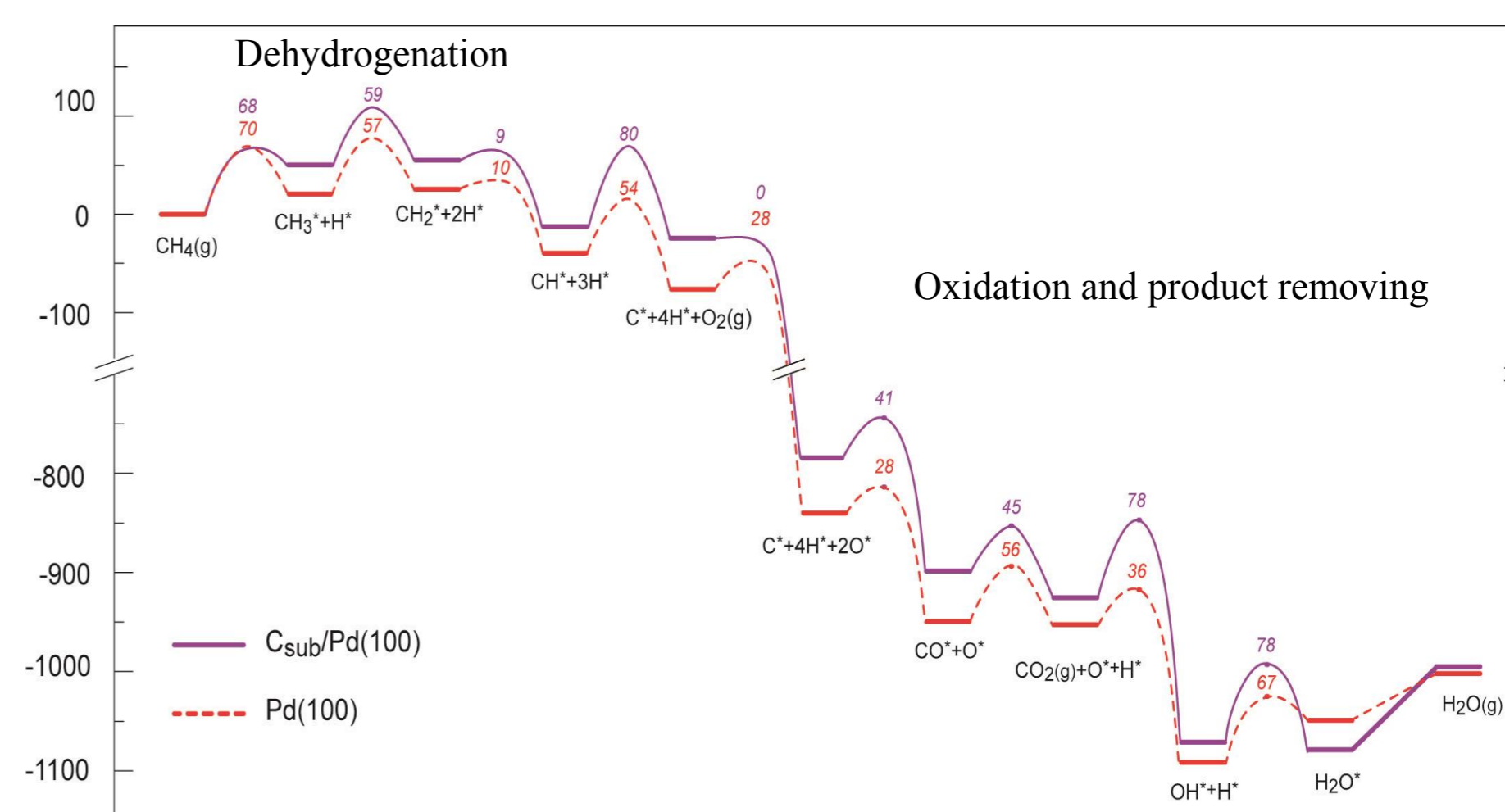
- ❖ Density functional theory (DFT)
- ❖ Plane-wave-based Vienna Ab initio Simulation Package VASP,
- ❖ Generalized gradient approximation (GGA) for the exchange-correlation functional PBE
- ❖ Projector augmented wave (PAW) method
- ❖ Kinetic energy cutoff of 415 eV
- ❖ Two bottom layers are fixed in bulk positions



2x2 5L-slab of Pd(100) surface and sites for carbon deposition

## Energy profile of the methane dehydrogenation

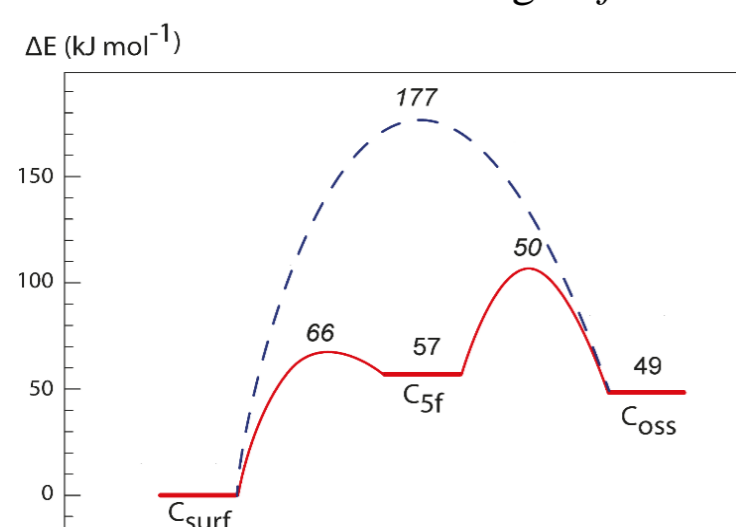
E in kJ·mol<sup>-1</sup> 32 reaction steps [5] → 17 elementary steps [6]



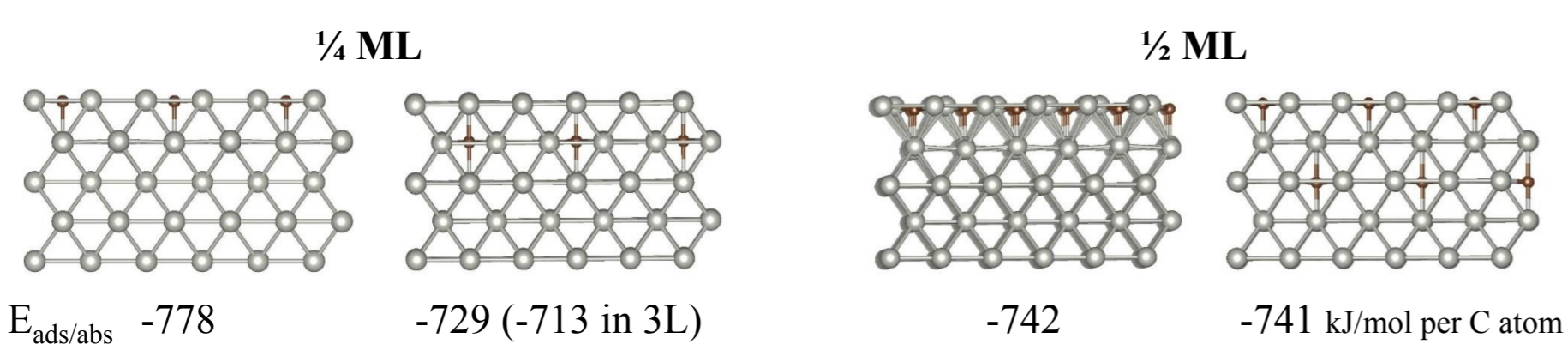
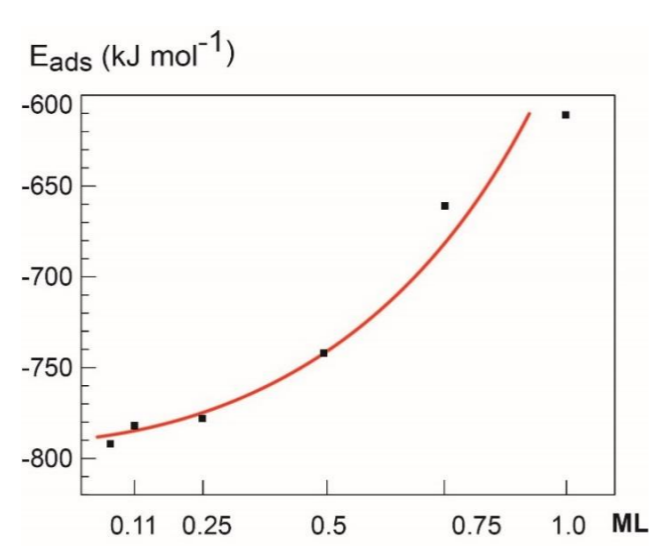
[5] M. Jørgensen. *ACS Catal.* 2016, 6, 6730. [6] E. A. Lashina et al. *J. Chem. Phys.* 2022.

## Formation of subsurface carbon

Energy diagram of C diffusion in Pd(100) surface from surface hollow site to oss through 5f.



Dependence of the adsorption energy on the coverage of C<sub>surf</sub>.



At > 0.5 ML C went into subsurface oss, at > 0.25 ML according to [3]. The C-C interaction becomes negligible at ~580 pm → deposition of C in the next neighboring surf sites and in oss across the Pd level [4].

[3] N. Seriani et al. *G. J. Chem. Phys.* 2010, 132(2), 024711.  
 [4] Y. He et al. *J. Phys. Chem. C* 2021, 125, 20930.

## Conclusions

- ❖ When surface coverage of C is greater than 0.5 ML, one can expect the stabilization and filling of the subsurface oss.
- ❖ The effect of C<sub>sub</sub> is manifested by lower adsorption energy of intermediates compared to the clean surfaces. The presence of C in the subsurface layer of Pd lowers the adsorption energies of the intermediates of the methane decomposition/oxidation reaction by up to 0.4 eV, excepting adsorption of water molecule. The endothermicity of the first (CH<sub>4</sub> → CH<sub>3</sub> + H) and last stages of methane decomposition (CH\* → C\* + H\*) increases by about 0.3 eV, transforming the latter from exothermic to weakly endothermic. The activation barrier of the last stage of decomposition also increases by 0.3 eV.
- ❖ The presence of C<sub>sub</sub> facilitates the removal of CO<sub>2</sub> and H<sub>2</sub>O from the surface.
- ❖ Thus, we can conclude that the dissolved carbon in the subsurface layers of palladium affects on its catalytic activity. It slows down the methane dehydrogenation on the Pd(100) surface, but facilitates oxidation of the intermediates and removal of products from the surface.