Size-dependent activity of platinum nanoparticles: theoretical insights from CO adsorption and methanol dehydrogenation

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Motivations

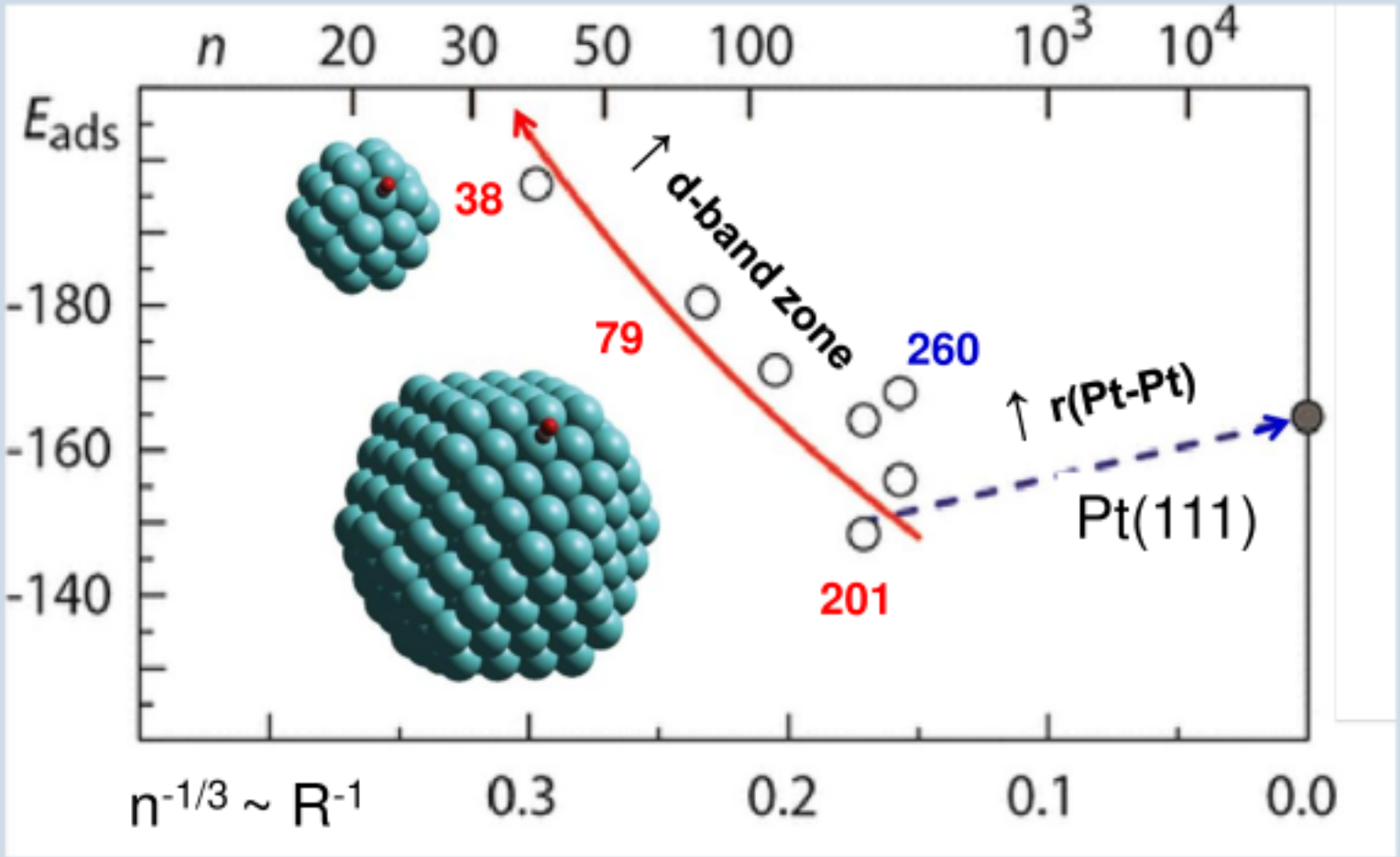
- Pt are catalysts of low alcohols decomposition, oxidation of alkenes.
- The methanol decomposition and oxidation proceeds most actively and selectively on defect Pt surfaces and Pt nanoparticles [1].
- Metallic nanoparticles are rich in undercoordinated Pt atoms at edges and vertices.
- In real catalysis nanoparticles of 1-100 nm size are normally used,
- Quantum modelling are in region before ~1 nm, n~10^2-10^3 atoms.
- Different metals may have different scalability region.

Goals

- With DFT methods, to study the effect of Pt_n cluster size (n = 38-314) on CO adsorption.
- To study the size effect of Pt_n clusters (n = 79, 201) on the activity in the methanol decomposition.

[1] V. V. Kaichev, I. P. Prosvirin, and V. I. Bukhtiyarov, *Kin. Kat.* **2014**, 88, 509.

CO adsorption energy on Pt clusters: non-scalable and scalable size regions



- Pt_n fcc-packed clusters
  - n = 38 ÷ 260
  - top sites for CO adsorption
- Two size regions
  - scalable (blue)

  n > ~200 (~1,7 нм)

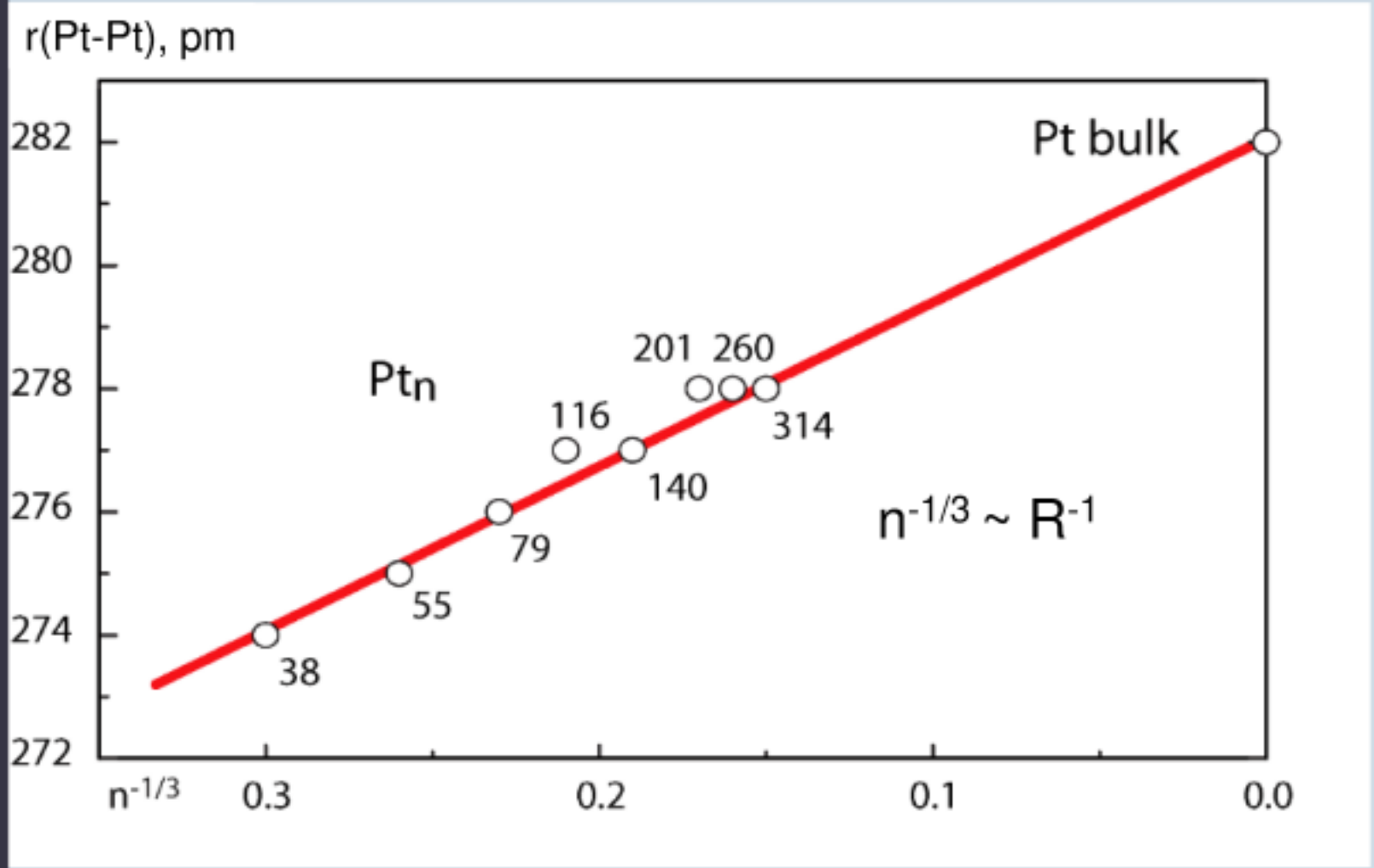
  $E_{ads} \sim n^{-1/3} \sim r(Pt\text{-}Pt)$
  - non-scalable (red)

  n < ~200 strong variation of E_{ads}

  E_{ads} ~ ↑d-band shift [Nørskov et al. *Phys. Rev. Lett.* **1996**, 76, 2141]

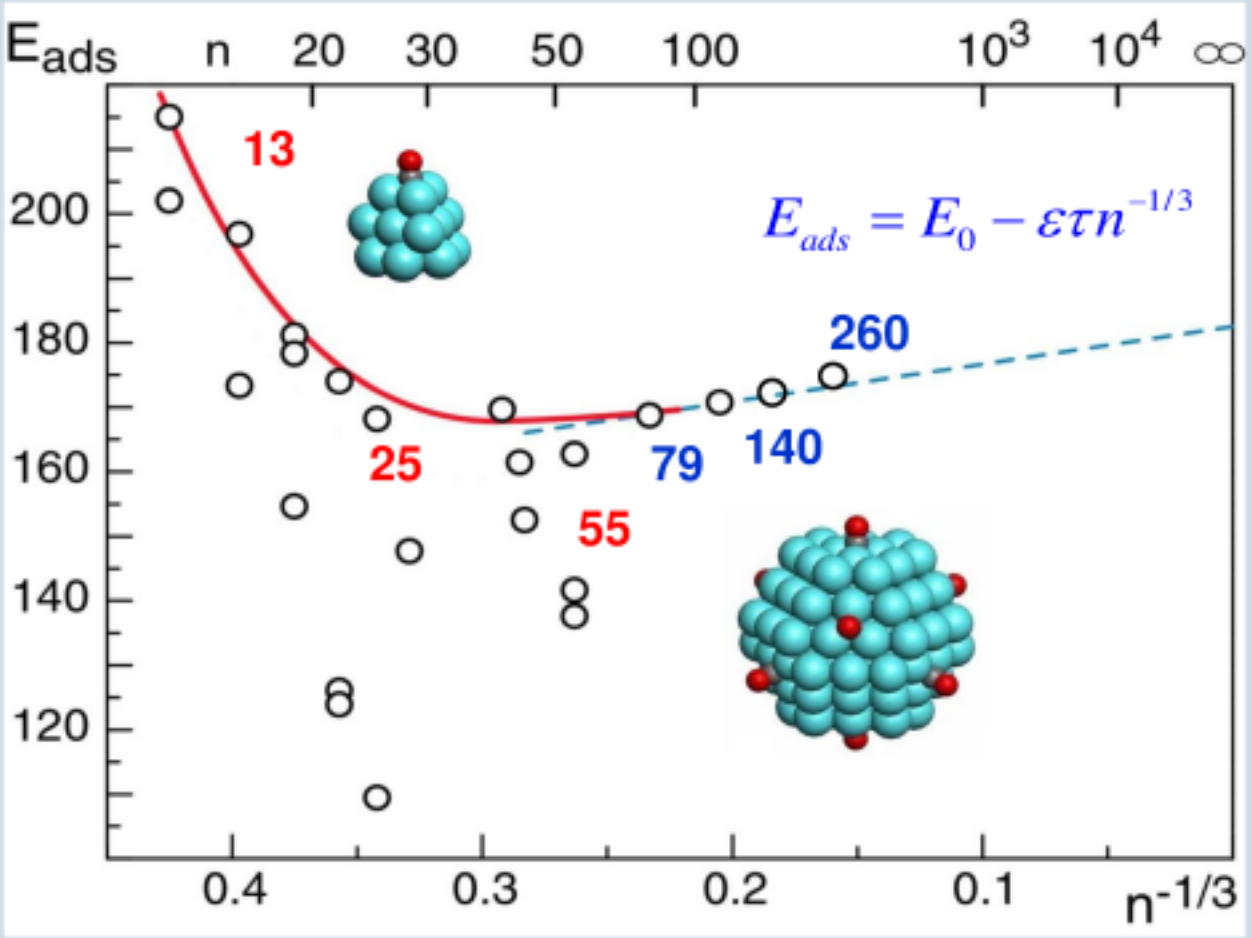
*Laletina, Mamatkulov, Shor, Kaichev, Yudanov, Genes, Rösch. J. Phys. Chem. C 2017, **121**, 17371.*

Size effect: : lattice contraction



- r(Pt-Pt) increases with cluster size to approach Pt bulk limit r_0
- Effect of lattice contraction
  - decrease of CO adsorption energy
  - weaker effect for edges than for facets

CO adsorption energy on Pd clusters: non-scalable and scalable size regimes



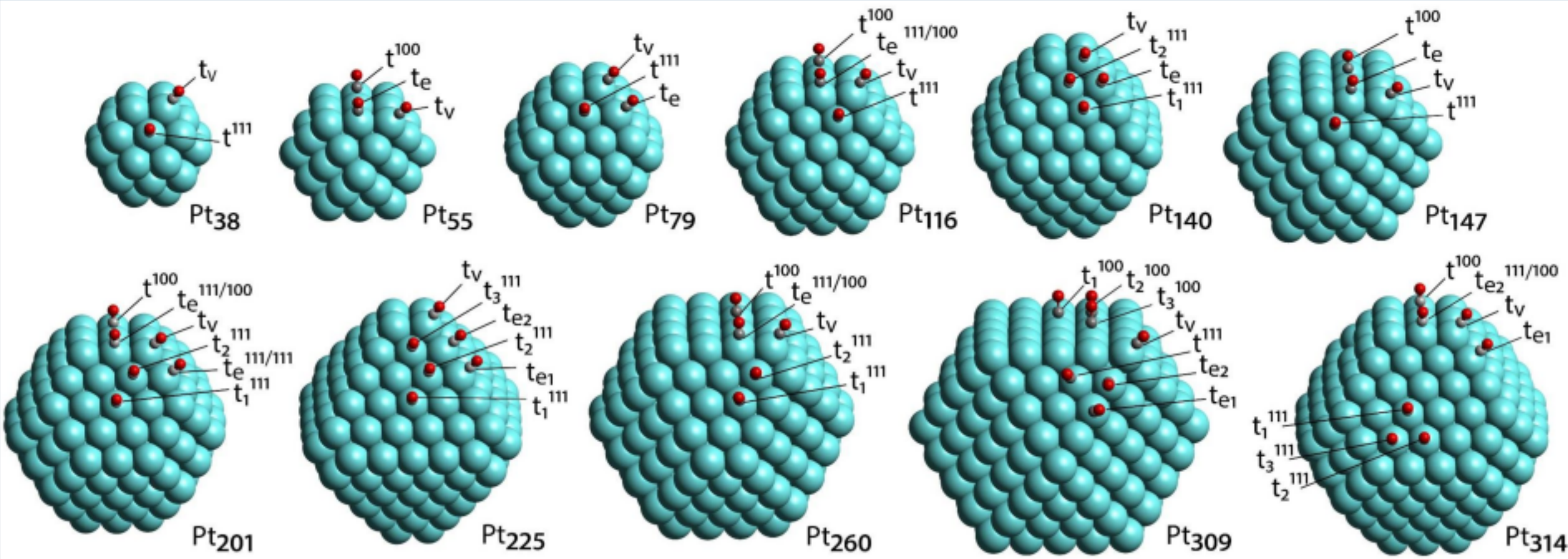
- ParaGauss
  - RPBE functional
  - 3-fold sites for CO adsorption
- Pd_n fcc-packed clusters
  - n = 13 ÷ 260
- Two size regions
  - scalable n > ~50
    $E_{ads} \sim n^{-1/3}$
  - non-scalable
    n < ~50 strong variation of E_{ads}

Yudanov, Genest, Schauermann, Freund, Rösch, Nano Lett. ***2012****, 12, 2134*

Goal 1

- With DFT methods, to study the effect of Pt_n cluster size (n = 38-314) on CO adsorption for **all** Pt sites.

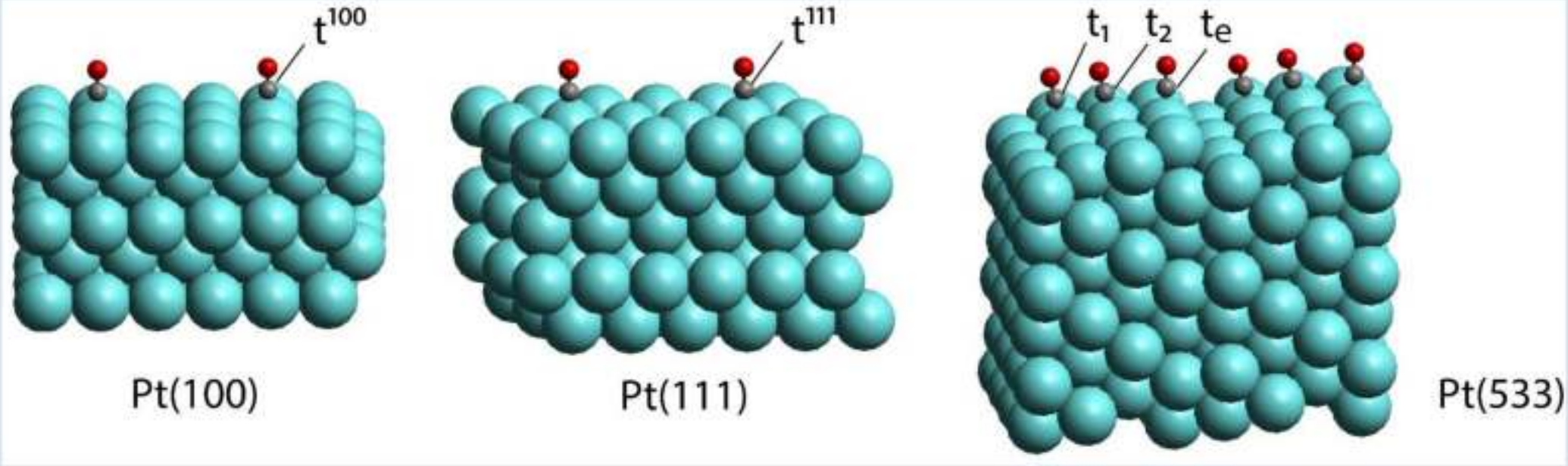
Models of NPs for CO adsorption



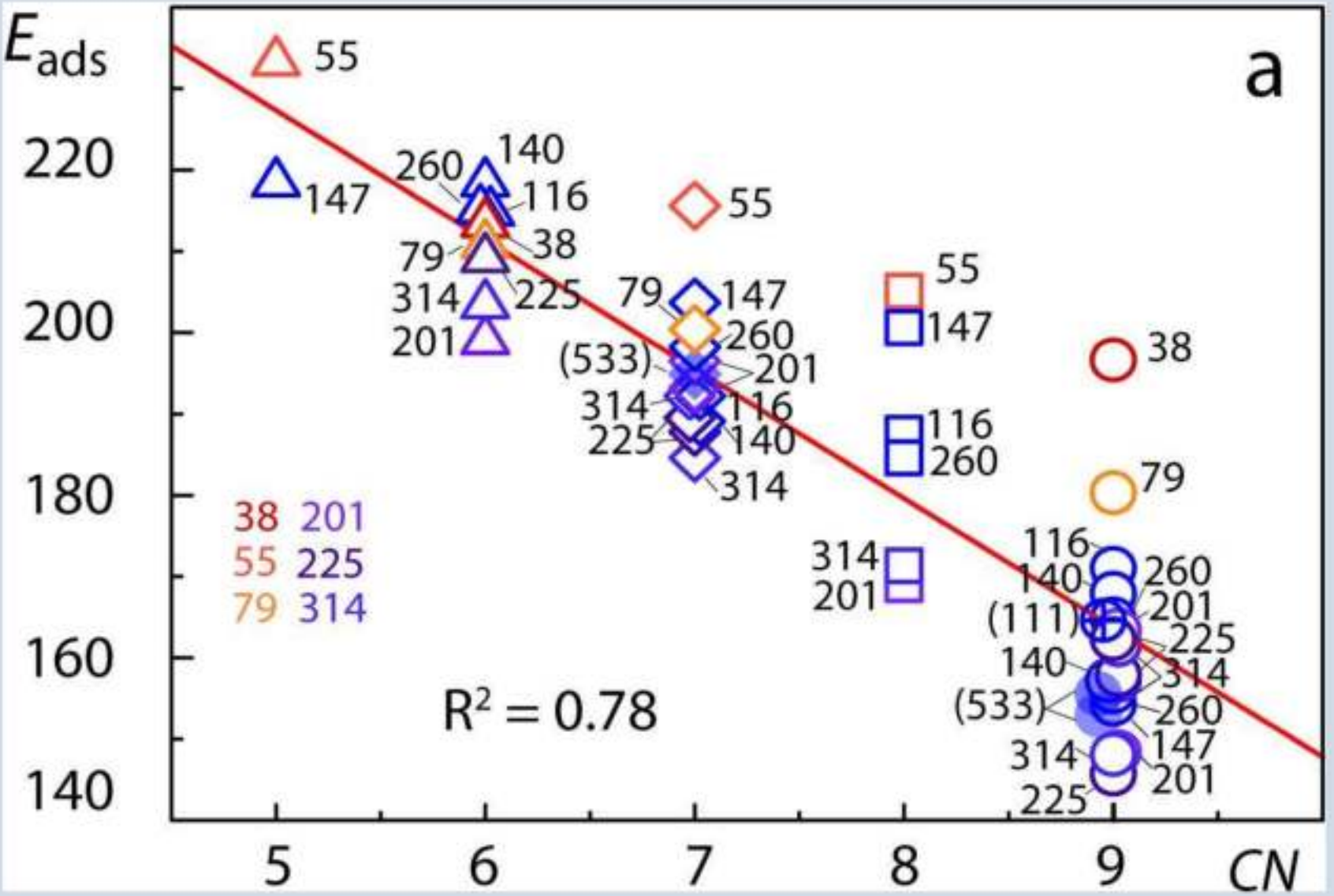
Truncated octahedrons and cuboctahedrons of 0.8-1.9 nm size

Methods and slab models

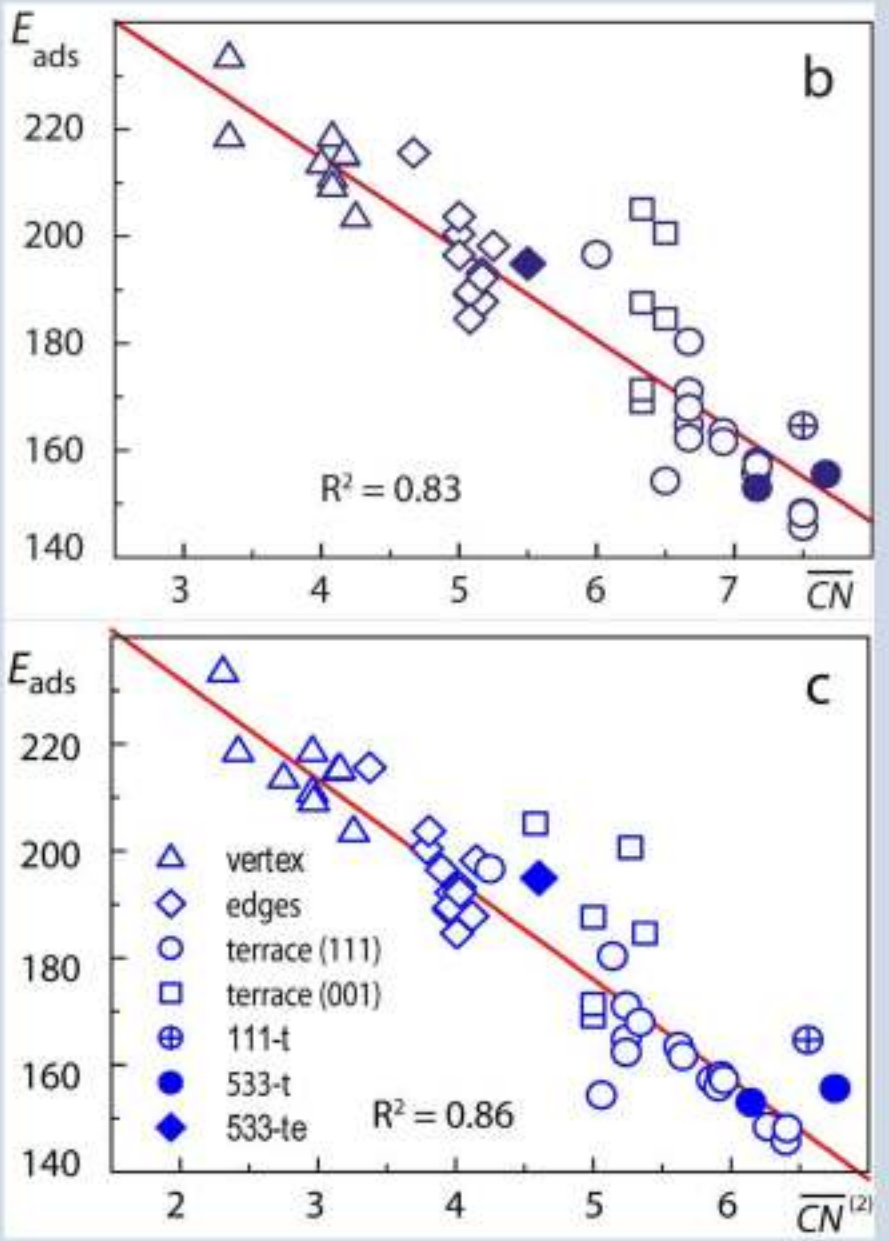
- Vienna Ab initio Simulation Package (**VASP**)
- **Plane-wave**-based projector augmented wave approach
- Density functional (**DF**) gradient-corrected exchange-correlation functional **PW91**
- Kinetic energy cutoff of **400 eV**
- **C1** symmetry



Dependence of E_{ads}(CO) on CN (coord. number)



Calculation of coordination numbers of metal atoms



1. Зависимость рассчитанных энергий адсорбции CO, E_{ads} (кДж/моль) от обобщенных координационных чисел, учитывающих среднюю координацию атомов, соседних с адс. центром

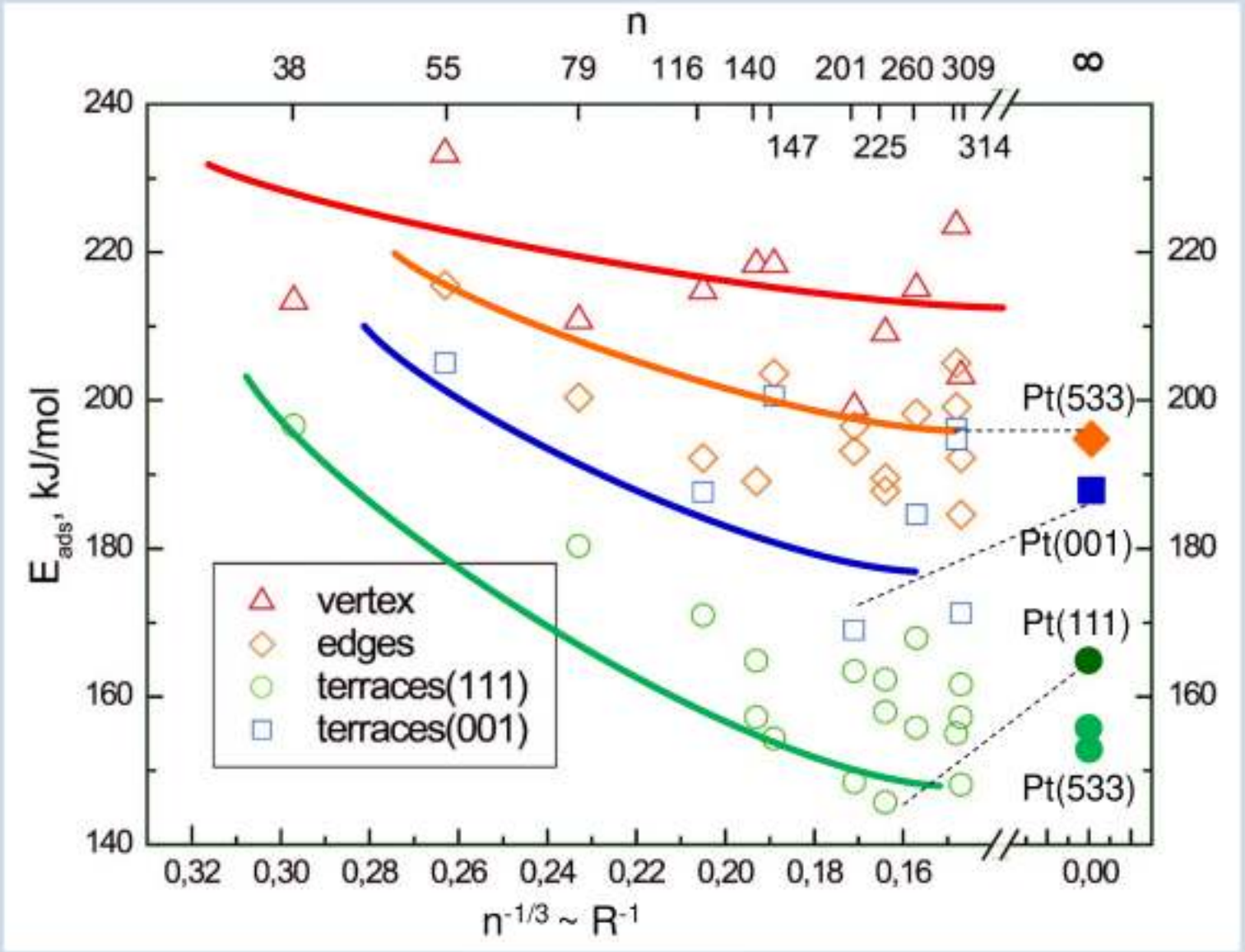
Calle-Vallejo et al.// Nat. Chem., 2015, 7, 403.

$$\overline{CN}(i) = \sum_{j=1}^{cn(i)} \overline{CN}(j) / cn_{\max}$$

2. Обобщенное координационное число 2-го порядка, учитывающее 3-ю корд. сферу. Адсорбция on-top была рассмотрена на атомах Pt, локализованных на гранях (окружности), ребрах (ромбы) и вершинах (треугольники) Pt_{79} (закрашенные) и Pt_{201} (пустые).

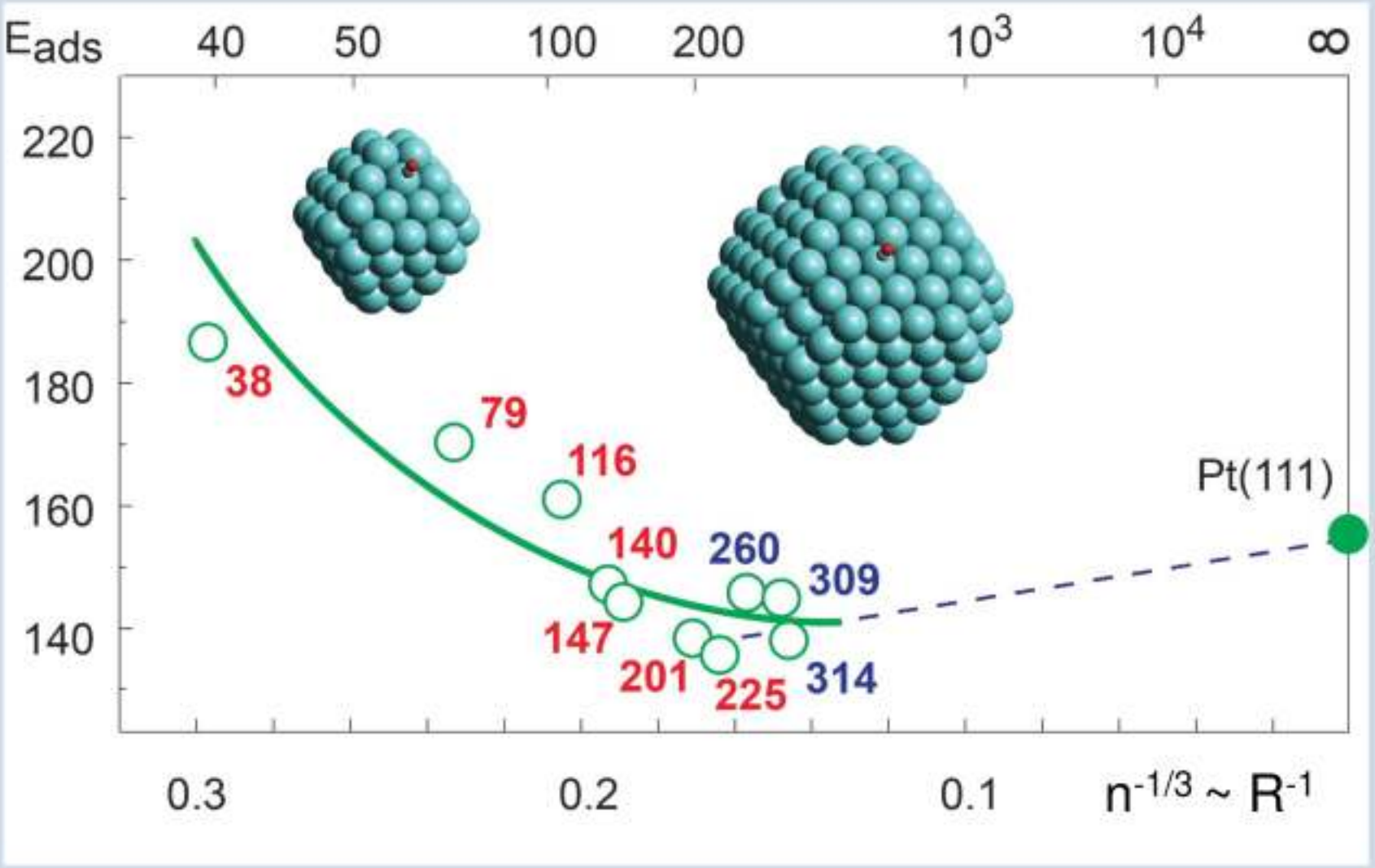
$$\overline{CN}^{(2)}(i) = \sum_{j=1}^{cn(i)} \overline{CN}(j) / cn(i)$$

CO adsorption energy on Pt_n clusters: (n = 38-314)



- Activity:
  - Vertex > edge > (100) terrace > (111) terrace
  - Cuboctahedrons (55, 147, 309 > octahedrons
- Energy value range:
  - 20-30 for small NPs and 70 kJ/mol for large ones
- Size effect:
  - mostly at the facets, less at the edges, and almost negligible at the vertices

CO adsorption energies on the (111) terrace of NPs

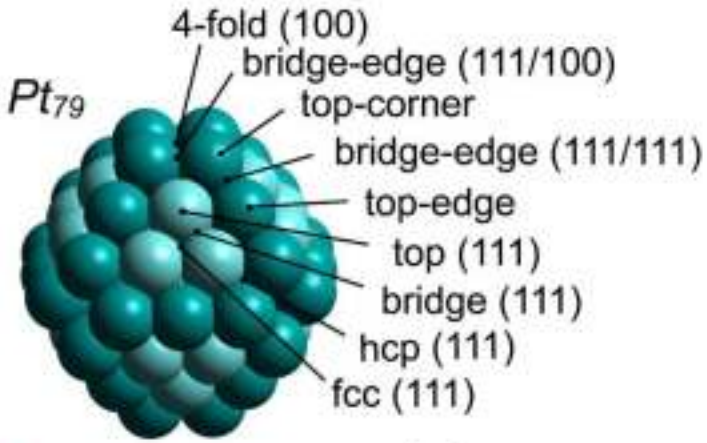


Goal 2

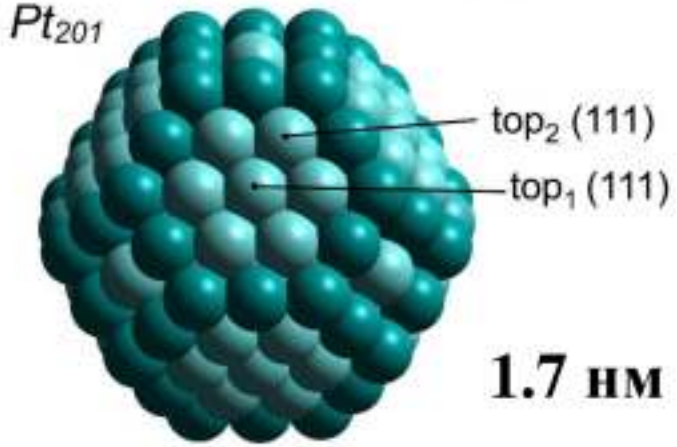
- To study the size effect of Pt_n clusters (n = 79, 201) on the activity in the methanol decomposition.

Methanol decomposition

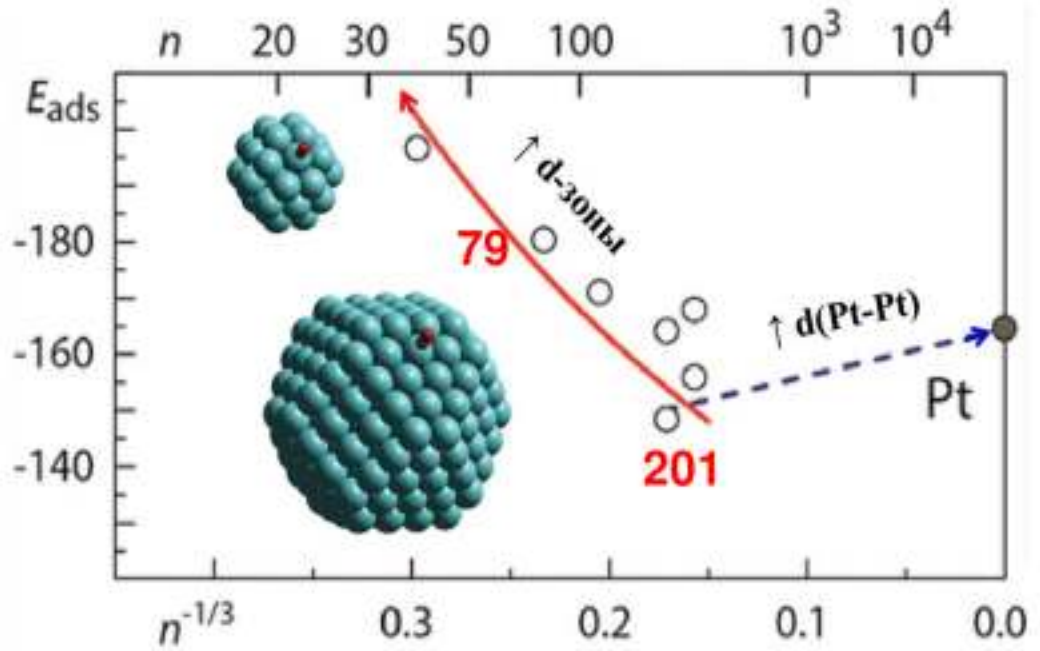
$CH_3O\text{-}H \xrightarrow{-H} CH_3O \xrightarrow{-H} CH_2O \xrightarrow{-H} CHO \xrightarrow{-H} CO$



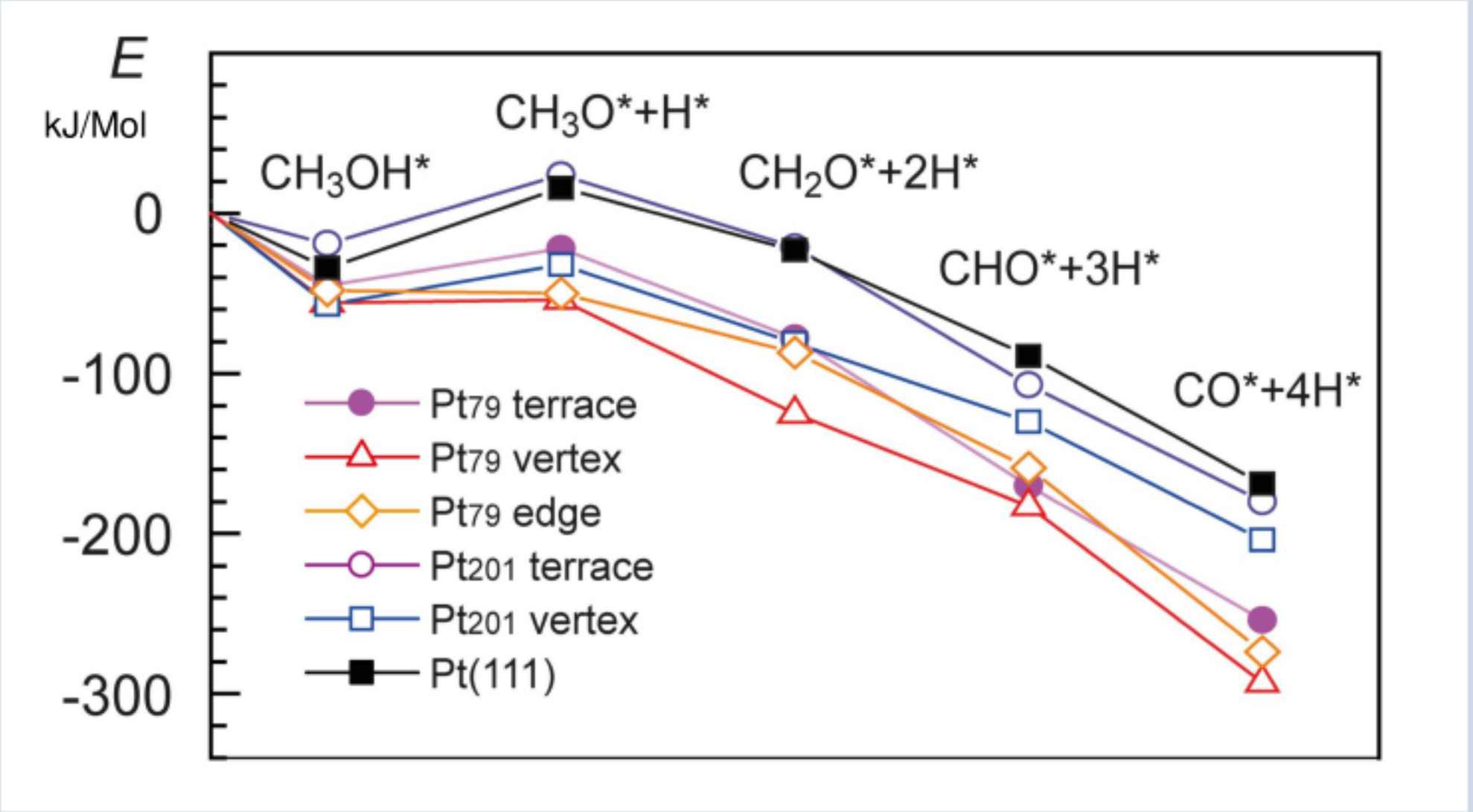
1.2 нм



1.7 нм

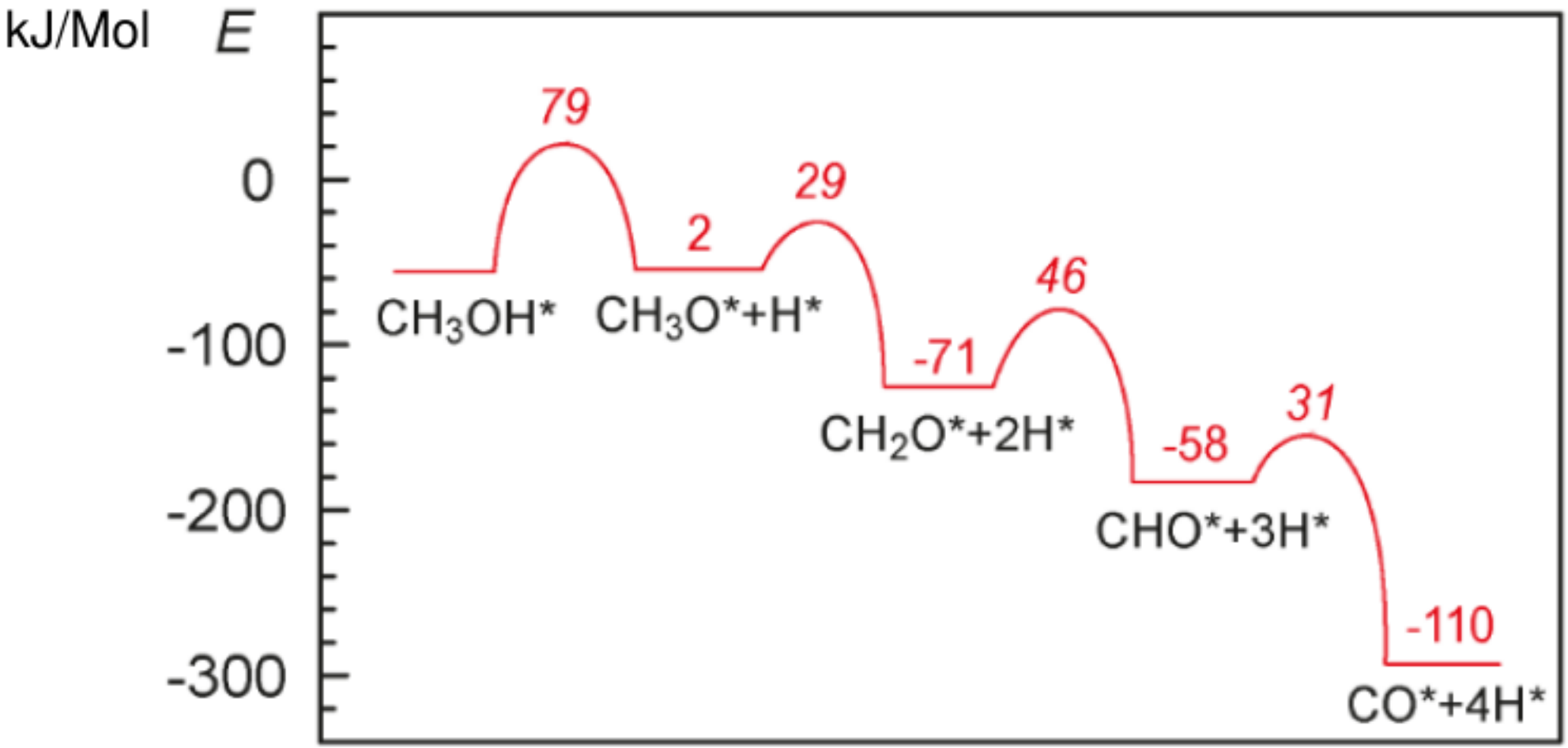


Energies of elementary reaction steps



S. S. Laletina, M. Mamatkulov, A. M. Shor, E. A. Shor, V. V. Kaichev, & I. V. Yudanov. Nanoscale, 2022, 14.

Energies of elementary reaction steps



S. S. Laletina, M. Mamatkulov, A. M. Shor, E. A. Shor, V. V. Kaichev, & I. V. Yudanov. Nanoscale, 2022, 14.

Summary

1) The **size effect** is detected mostly at the facets, less at the edges, and almost negligible at the vertices. Moreover, as the cluster grows, the value range between the most active and the least active centers increases. While for small clusters it is 20-30 kJ/mol, for large clusters it reaches 70 kJ/mol. Cuboctahedral clusters (less stable according to Wulffe's rule) are more active than octahedral ones.
2) **Two opposite dependencies** of CO adsorption energy on particle size were found: 1) for particles with n<201 a sharp increase in adsorption energies with decreasing particle size associated with an upward shift of the transition metal d-orbitals; 2) for particles with n>201 a smooth increase in adsorption energies with increasing particle size up to the infinite surface Pt(111) due to increasing distances of Pt-Pt lattice. To explain the dependences, a new method of calculating the coordination numbers of metal atoms, taking into account their second and third coordination spheres, was proposed.
3) The study of the **methanol decomposition** confirms this observation. The vertices of clusters 79 and 201 are the most active. Whereas the terrace of cluster Pt_{201} exhibits lower activity in the adsorption of CH_xO intermediates comparable to the infinite surface of Pt(111).

Aknowledgment

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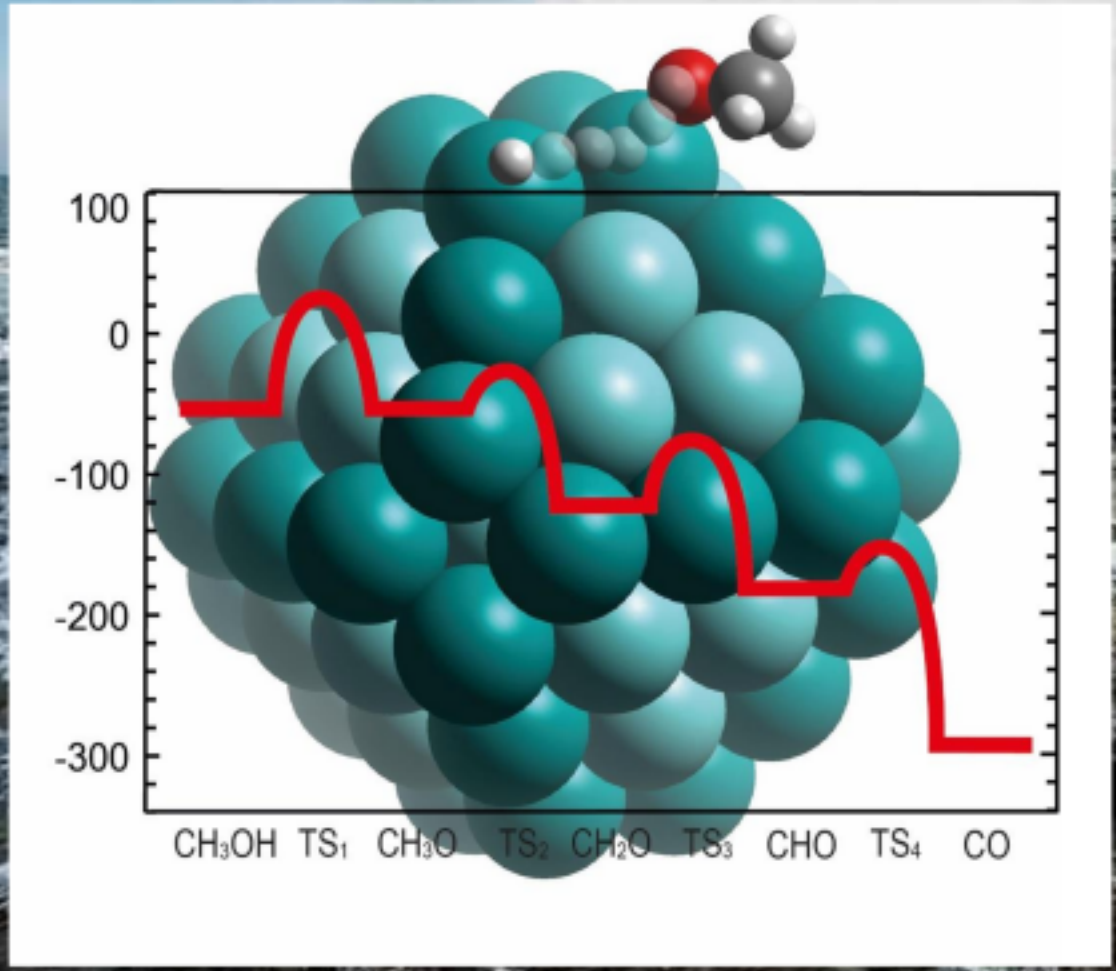
- RFBR (Russian Foundation for Basic Research), grant 16-33-00578

Computing resources:

- Siberian Supercomputer Centre (www2.sscc.ru)
- Krasnoyarsk Regional Research Equipment Centre

Thank you for your attention!



Tobizin cape, Russian Island, Vladivostok