X International Voevodsky Conference "Physics and Chemistry
of Elementary Chemical Processes" (VVV-2022)

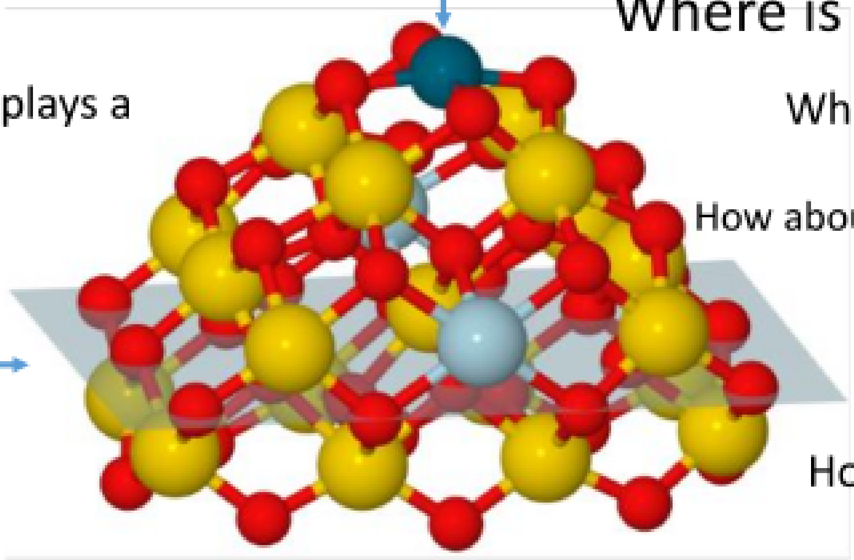
Palladium atoms and clusters at ceria nanoparticles: a DFT study

Shor E.A., Shor A.M., Nasluzov V.A.

*Institute of Chemistry and Chemical Technology SB RAS,
Krasnoyarsk, Russia*

September, 6, 2022

Single-atom catalyst (SAC)



Isolated single atom

Oxide support plays a role of ligand

Where is the metal atom located?

What is its coordination number?

How about its thermal stability and mobility?

How is to identify single-atom site?

Are properties of SAC correlate with those of homogeneous and heterogeneous systems?

SACs efficiency approaches that of homogeneous systems

Pacchioni G. et al. *Acc. Mater. Res.* 2022

Pd/ceria catalysts

Why palladium?

- CO oxidation to CO_2
- Water-Gas-Shift reaction $CO + H_2O = CO_2 + H_2$
- solid oxide fuel cell
- Conversion of automobile exhaust gases

Why ceria?

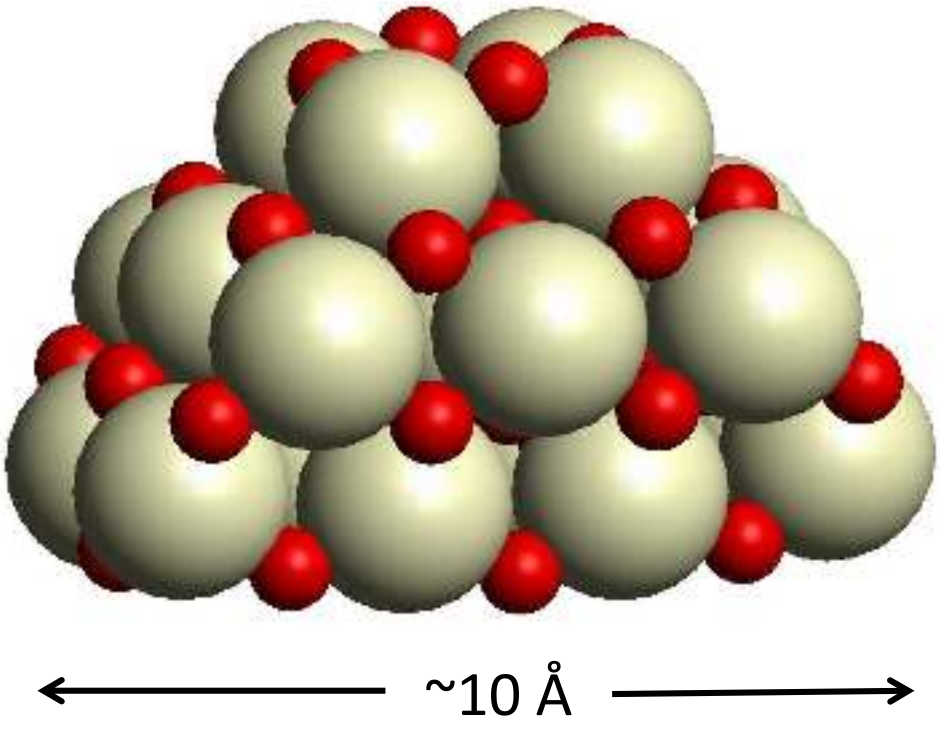
- High mobility of lattice oxygen (energy of O removal – 2.3-2.6 eV)
- Reduction/oxidation Ce^{4+}/Ce^{3+} switch

$$O^{2-} + Ce^{4+} \rightarrow O_V + 2Ce^{3+}$$

$$Me^0 + Ce^{4+} \rightarrow Me^{n+} + nCe^{3+}$$

- Strong metal-support interaction (energy of metal trapping – 2-4 eV)
- Nanostructuring affects catalytic performance (enhancement by 2 times of CO oxidation at Au/nano-CeO_2)

Nanosized Particle $Ce_{21}O_{42}$

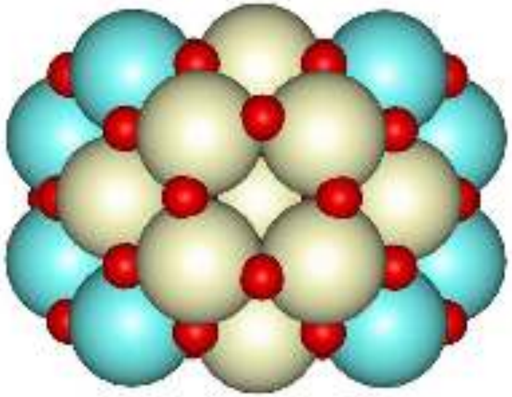


● Ce^{5c}

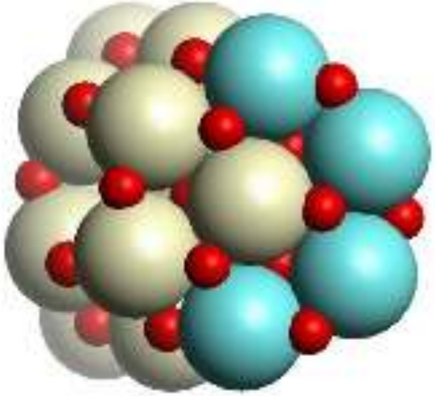
● O^{2c}

● Ce^{6c}

● O^{3c}



Top view, CeO_2 {100}



Side view, CeO_2 {111}

Migani, Vayssilov, Bromley, Illas, Neyman, Chem. Commun. 46 (2010) 5936.

Computational details

- Vienna Ab-initio Simulation Package (VASP) code
- Perdew-Wang (PW91) exchange-correlation functional
- Projected augmented wave (PAW) formalism
- Kinetic energy cut off of 415 eV
- Hubbard U term = 4 to describe localized Ce 4f states
- Unit cell size 20 × 20 × 20 Å

Open questions

1) What about stability of atomic and few-atom Pd particles at ceria surfaces?
2) How is to identify single-atom Pd species adsorbed at ceria?
3) How mobility of oxygen is changed upon adsorption of Pd particles on ceria?
4) Whether the transformation and denucleation of Pd clusters is feasible?

Structure and Adsorption energy

Regular CeO_2 (100) surface

r(Pd-O)=205 pm
CN(Pd)=4
q(Pd)=+2

Pd

E_{ad}=**-4.25; 2(Ce^{3+})**

Pd_2

E_{ad}=**-4.45; 2(Ce^{3+})**

Pd_3

E_{ad}=**-4.14; 2(Ce^{3+})**

Pd_4

E_{ad}=-**3.57; 2(Ce^{3+})**

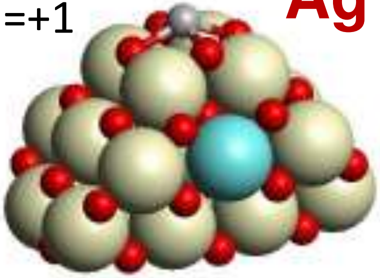
Trend to horizontal Pd structures

● Reduced cerium ion Ce^{3+}

Pd species are oxidized and strongly bound

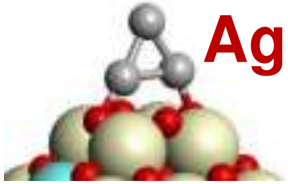
r(Ag-O)=236 and 242 pm
CN(Ag)=4
q(Ag)=+1

Ag



E_{ad}=**-2.17; 1(Ce^{3+})**

Ag_3



E_{ad}=**-2.91; 1(Ce^{3+})**

Ag_4

E_{ad}=**-2.86; 2(Ce^{3+})**

Calc. energy of adsorption (in eV):
(Os^{6+})= -9.7
(Ru^{3+})= -8.0
(Pt^{2+})= -6.7
(Cu^{+})= -4.0
(Au^{+})= -2.6

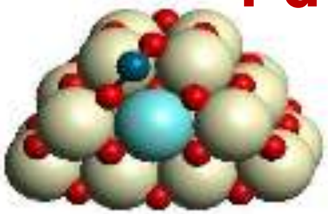
Catal. Sci. Technol., 2016, 6, 6806.

Nasluzov et al. Surface Science, 2019, V.681, P. 38–46.

Regular CeO_2 (111) surface

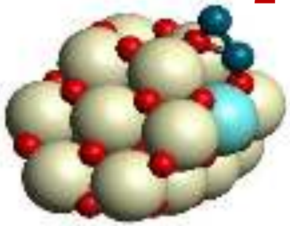
r(Pd-O)=206-210 pm
CN(Pd)=2

Pd



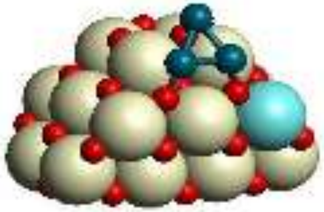
E_{ad}=**-1.90; 1(Ce^{3+})**

Pd_2



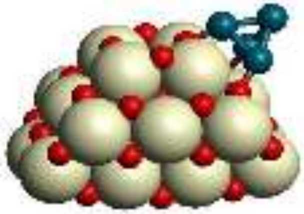
E_{ad}=**-2.69; 1(Ce^{3+})**

Pd_3



E_{ad}=**-2.62; 1(Ce^{3+})**

Pd_4



E_{ad}=**-2.76; 1(Ce^{3+})**

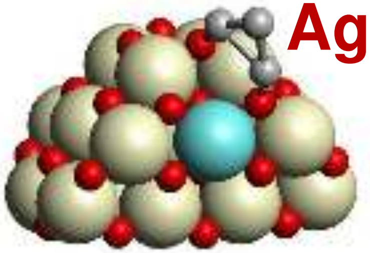
Weaker bonding by ~1-2 eV than at {100} facet for both metals

r(Ag-O)=223; 2×247 pm
CN(Ag)=3

Ag

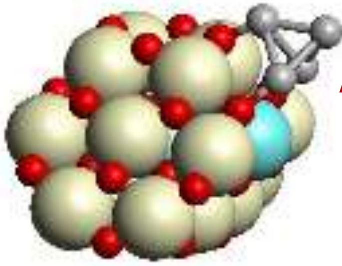
E_{ad}=**-1.22; 1(Ce^{3+})**

Ag_3



E_{ad}=**-2.47; 1(Ce^{3+})**

Ag_4



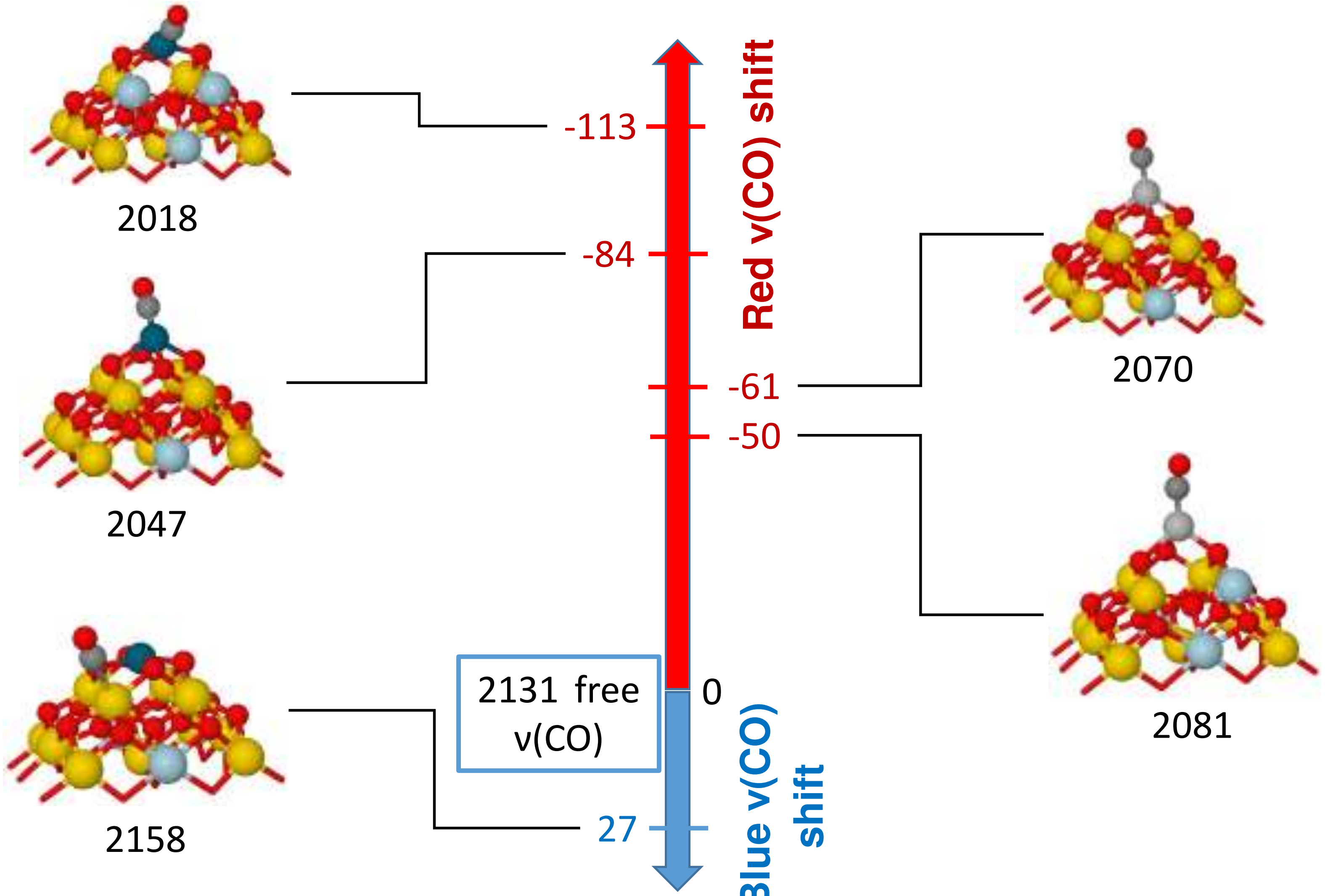
E_{ad}=**-1.99; 2(Ce^{3+})**

Nasluzov et al. Surface Science, 2019, V.681, P. 38–46.

Site identification with CO frequencies

Experiment for Pd/CeO_2: red shift at 10-123 cm^{-1}
Boronin, Cat. Today (2009) ; Spezzati, Appl Cat. B (2019)

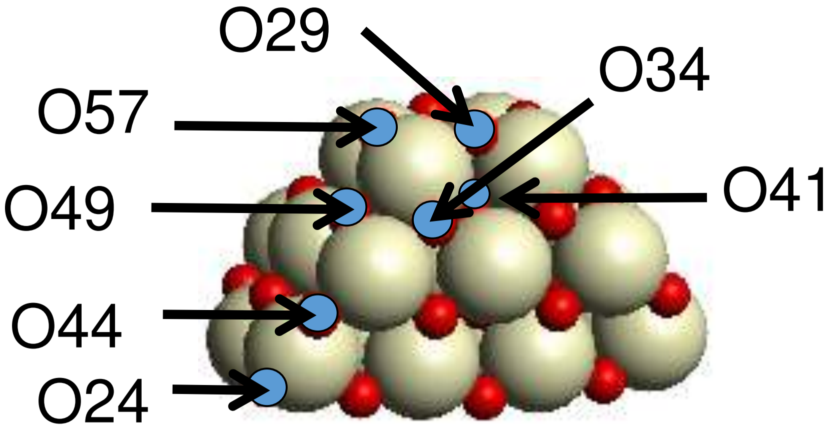
Pd **Ag**



Nasluzov et al. Materials, 2021, V.14(22), 6888.

Oxygen vacancy formation

Oxygen vacancy formation in pristine $Ce_{21}O_{41}$



	$E_f(O_{vac})$	CN		**$E_f(O_{vac})$**	CN
O29	**1.56**	2	O44	**2.33**	2
O41	**1.72**	4	O34	**2.69**	3
O24	**1.84**	2	O49	**2.89**	3
O57	**1.87**	2			

CN – coordination number

O vacancy formation leads to reduction of two Ce^{4+} ions to Ce^{3+}

Calc. values for infinite surfaces (HSE)
CeO_2 (100) = 2.3 eV [1]
CeO_2 (111) = 2.65; 3.10 eV [2]

[1] Migani et al, J. Mater. Chem. 20 (2010) 10535.
[2] Sauer, Phys. Rev. Lett. 102 (2009) 026101.

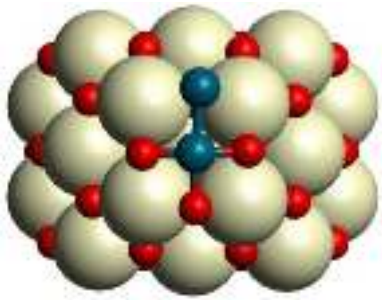
Extra-framework Pd species

O vacancy is created in the most favored O29 position
(values in parenthesis for O vacancy in O41 position)

Pd

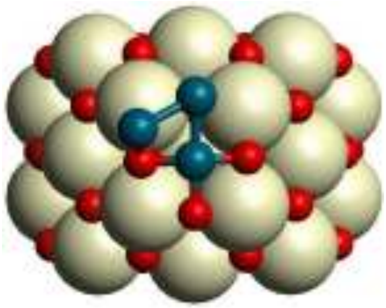
2.94
(2.33)

Pd_2



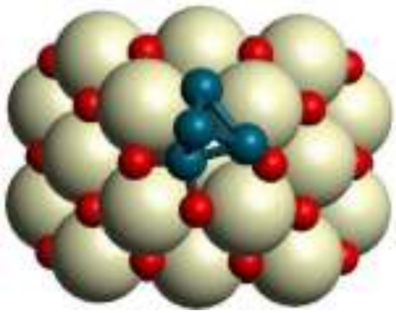
2.02
(2.02)

Pd_3



2.01
(2.41)

Pd_4



2.00
(1.97)

O vacancy formation energy ↑ compared to metal-free particles (**1.56 eV**)

Extra-framework Pd species disfavor O release from ceria

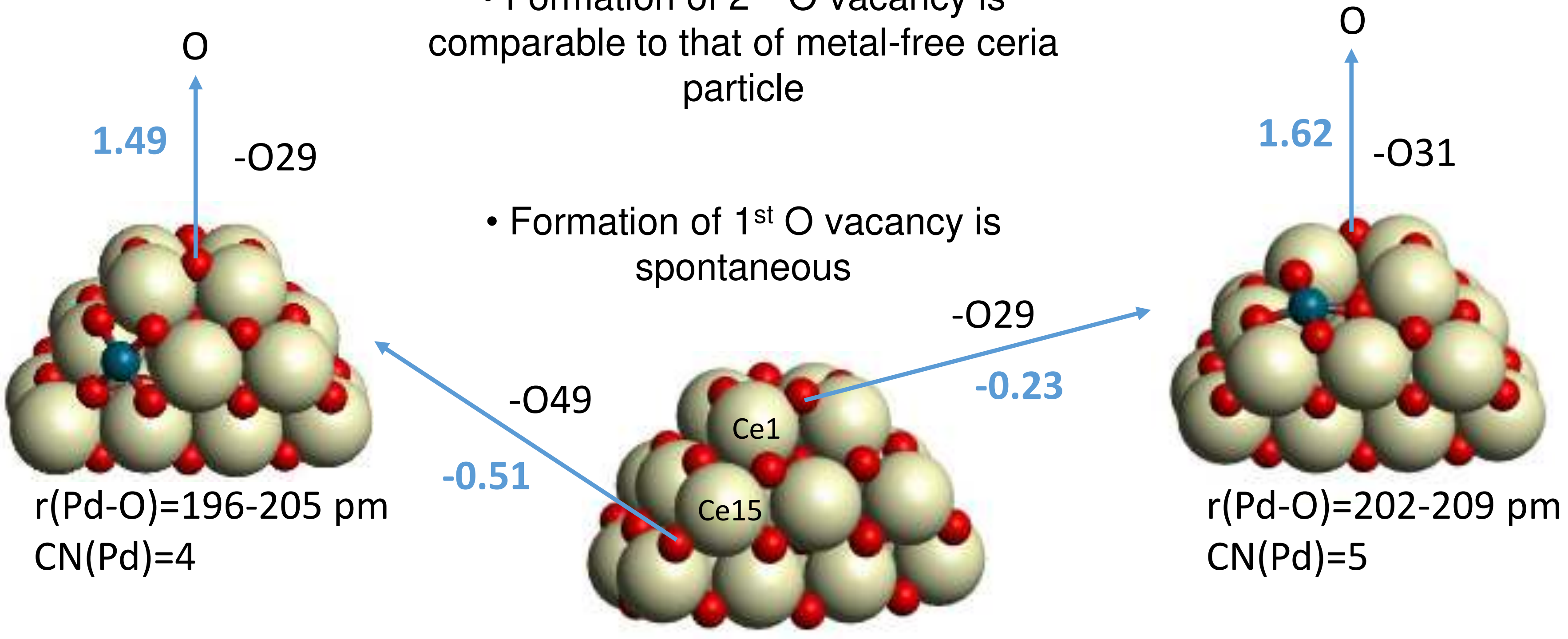
Intra-framework Pd species

Pd in position 15

Pd in position 1

- Formation of 2nd O vacancy is comparable to that of metal-free ceria particle

- Formation of 1st O vacancy is spontaneous



r(Pd-O)=196-205 pm
CN(Pd)=4

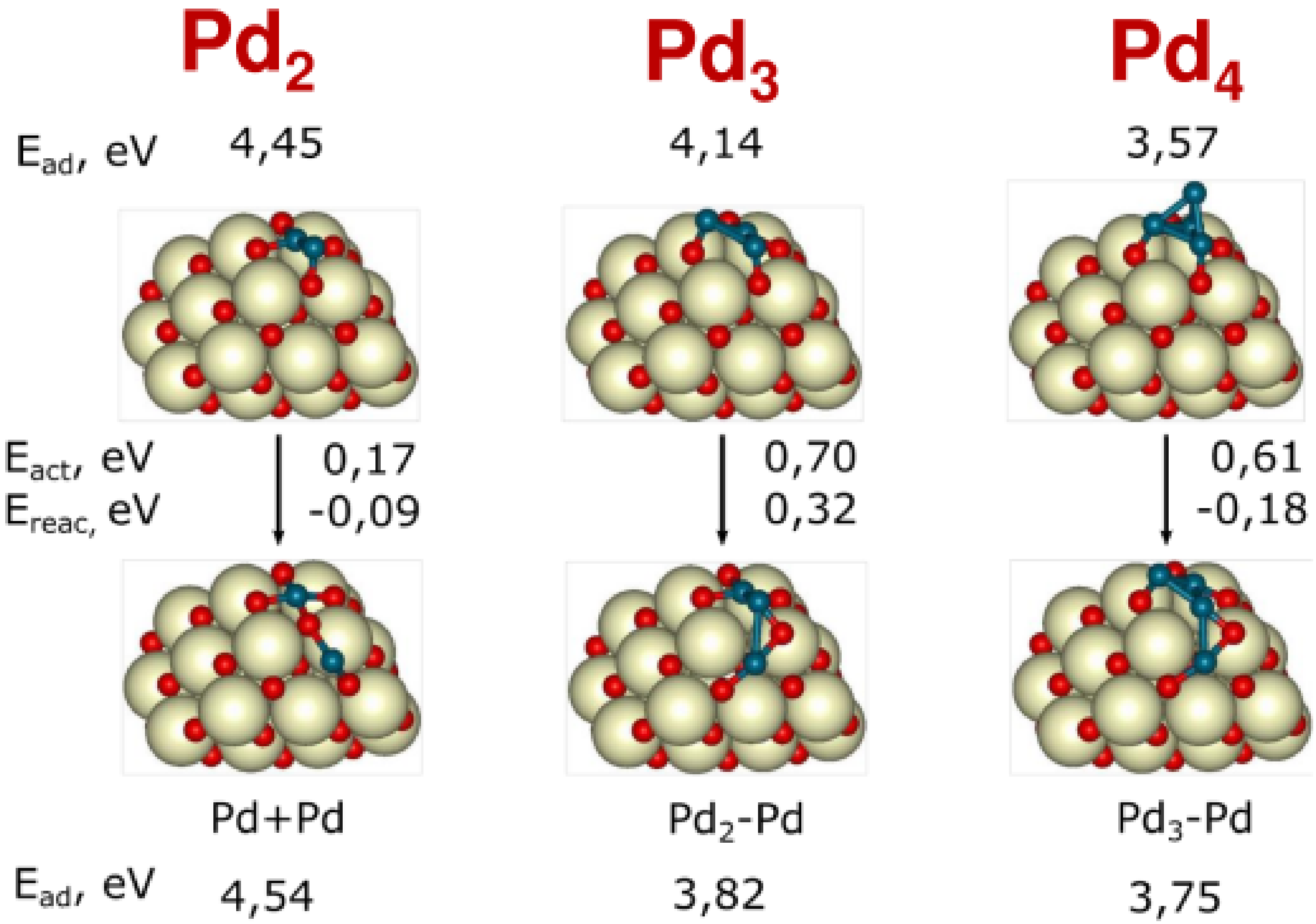
CN(Ce) = 5
r(Ce-O)=224-238 pm

r(Pd-O)=202-209 pm
CN(Pd)=5

Intra-framework Pd species favor O release from ceria

Cluster structure stability

Deformation of Pd_n (n=2-4) particles



	Pd_2	Pd_3	Pd_4
E_{ad}, eV	4,45	4,14	3,57
E_{act}, eV	0,17	0,70	0,61
E_{reac}, eV	-0,09	0,32	-0,18
	Pd+Pd	Pd_2-Pd	Pd_3-Pd
E_{ad}, eV	4,54	3,82	3,75

Stability of distorted clusters is high
Migration barriers for Pd atoms are low

Conclusions

1) Extra stabilization of monoatomic Pd and few-atomic Pd_n species at {100} facet of ceria nanoparticle with formation of local square-planar PdO_4 fragment was calculated. Adsorption at {111} is by 1-2 eV weaker and comparable to Ag_n particles.

2) Ceria-supported Pd atoms at {100} can be probed by adsorbed CO molecule. Calculated red shift of CO frequency at 84-113 cm^{-1} agrees with experimental values.

3) Adsorbed at ceria $Ce_{21}O_{42}$ nanoparticle extra-framework Pd species disfavor release of lattice oxygen by 0.5 eV. Opposite, intra-framework Pd atoms leads to spontaneous removal of one lattice O atom from nearest Pd environment.

4) Few-atom Pd particle adsorbed at {100} facet of $Ce_{21}O_{42}$ nanoparticle are prone to deformation due to migration of one Pd atom to {111} facet. Distorted forms are created with small activation barriers and thermodynamically stable.

Acknowledgements

Colleagues and co-authors:

Aleksey M. Shor
Vladimir A. Nasluzov
Konstantin M. Neyman

Computational resources:

Siberian Supercomputer Center
Lomonosov Supercomputer Center

Tnahk you for attention!