Финансирано от Европейския съюз
NextGenerationEU

SUMMIT
SOFIA UNIVERSITY MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

Национален план за възстановяване и устойчивост
НА РЕПУБЛИКА БЪЛГАРИЯ

SOFIA UNIVERSITY – MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

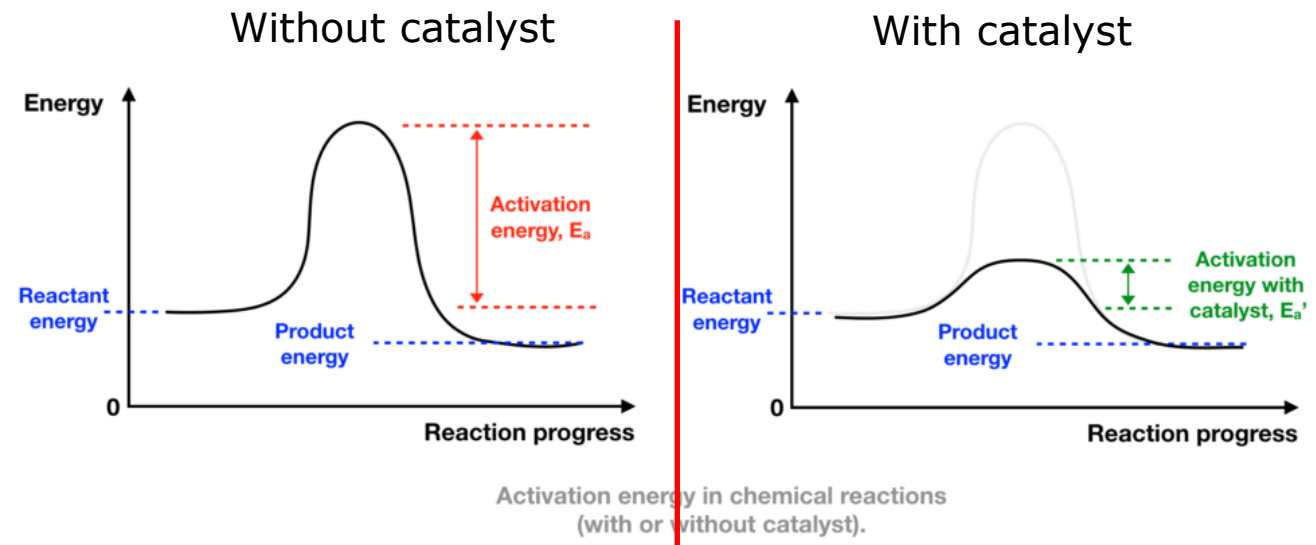
Quantum chemical modeling of catalytic systems and reactions on them

prof. Hristiyan Aleksandrov

Scientific group: 3.1.5 „Computational Heterogeneous Catalysis“

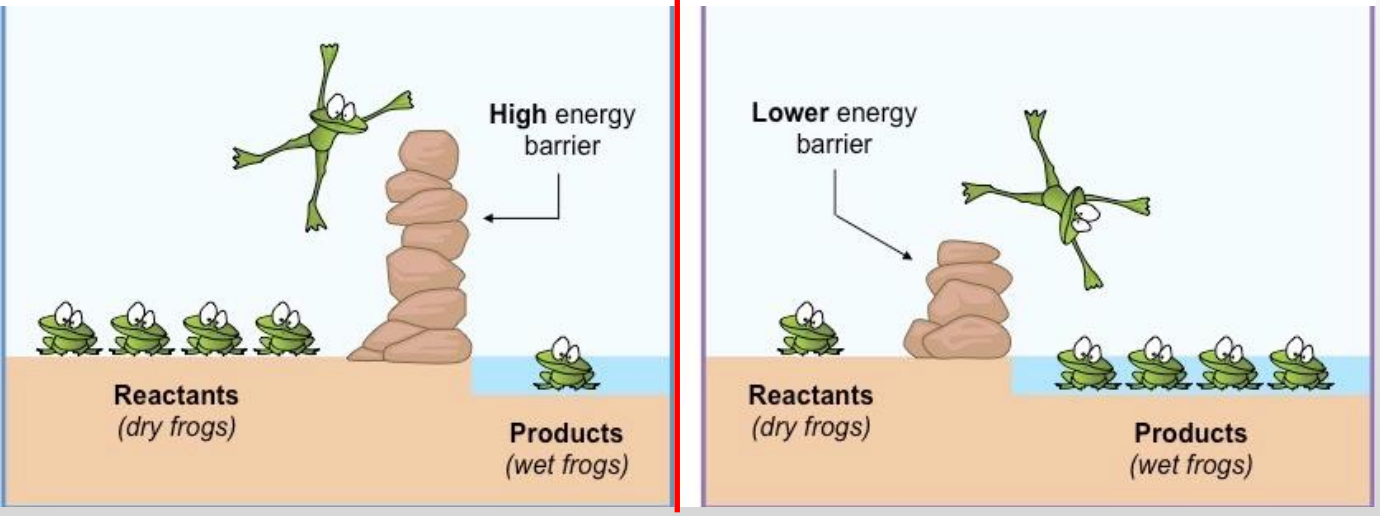
Договор BG-RRP-2.004-0008 за финансиране на проект „СОФИЙСКИ УНИВЕРСИТЕТ – МАРКЕР ЗА ИНОВАЦИИ И ТЕХНОЛОГИЧЕН ТРАНСФЕР (SUMMIT)“ по стълб 2 „Създаване на мрежа от изследователски висши училища“ в рамките на компонент „Иновативна България“ от Национален план за възстановяване и устойчивост към програмата за ускоряване на икономическото възстановяване и трансформация чрез наука и иновации

Catalysts



Activation energy in chemical reactions (with or without catalyst).

https://yugal.me/activation-energy-and-catalysts/



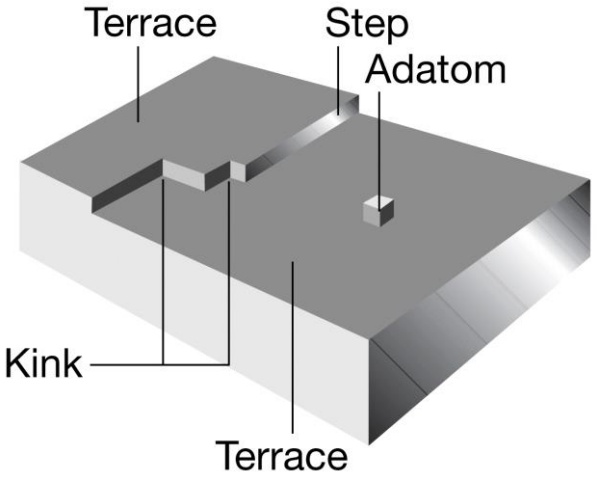
- Increase the rate of chemical reactions without themselves being consumed
- Lower the activation energy
- Help the reactions to occur under favorable conditions (P and T), increasing the yield and reducing the cost of the product
- More than 80% of industrial processes are expedited (at least in part) by catalysis

https://ib.bioninja.com.au/higher-level/topic-8-metabolism-cell/untitled-6/activation-energy.html

Computational heterogeneous catalysis

- Computational catalysis can help to:
  - Determine the structure of the catalysts and outline the catalytic sites
  - Find the most plausible pathway of the catalytic transformations
- Complications:
  - Defects and irregularities on the catalytic surface
  - Multicomponent catalysts
  - Impurities and spectator species on the surface

Wilde, Schauermann, Freund et al.
Angew. Chem. Int. Ed. 47 (2008) 9289



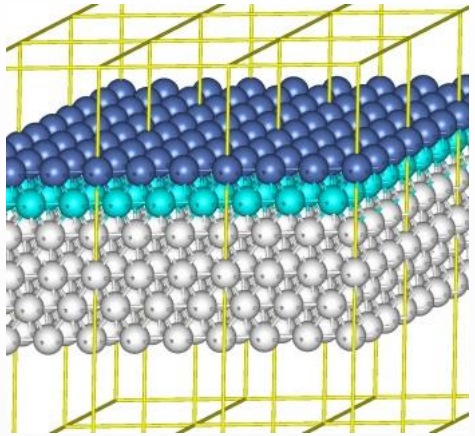
Solar, Blanco, Vallone, Sapag,
Natural Gas 2010, 205–244.

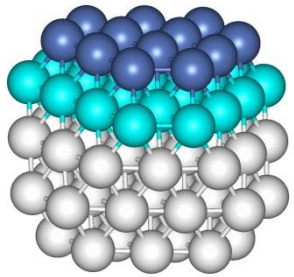
Scientific group: 3.1.5 „Computational Heterogeneous Catalysis“

In the focus of the project is quantum-chemical modeling of catalytic materials and processes which can be used:

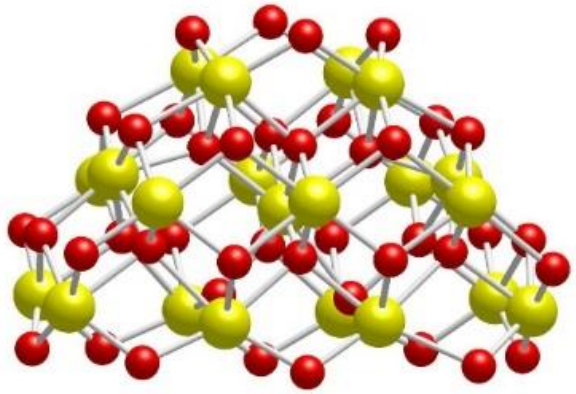
- To convert the harmful automotive exhaust gases (CO, NO_x, and hydrocarbons) into non-toxic CO_2, H_2O, and N_2
- For storage of harmful and greenhouse gases as CO_2, CH_4, and NO_x
- To produce green hydrogen
- For nitrogen fixation processes
- We will pay special attention to the possibility to reduce the amount of precious metals in these catalysts, but simultaneously the reactivity and selectivity to be retained and even enhanced
- The results of this project will help to be elaborated better and cheaper catalysts for cleaner environment and production of green energy

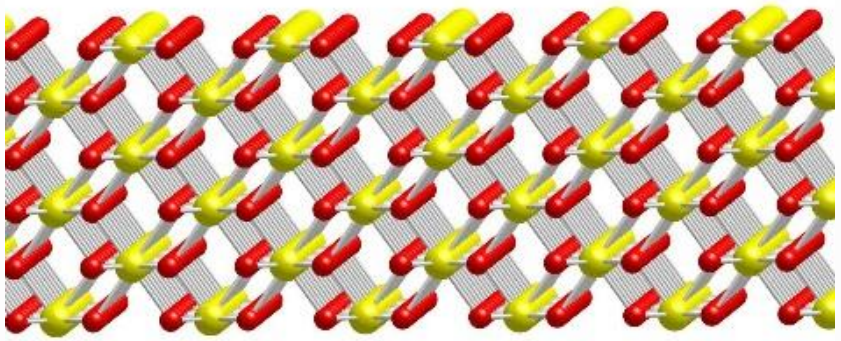
Modeled materials with catalytic applications



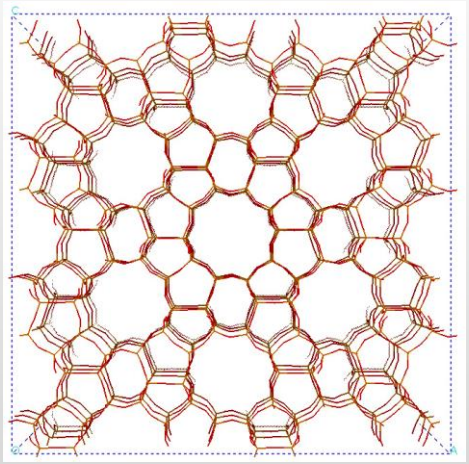


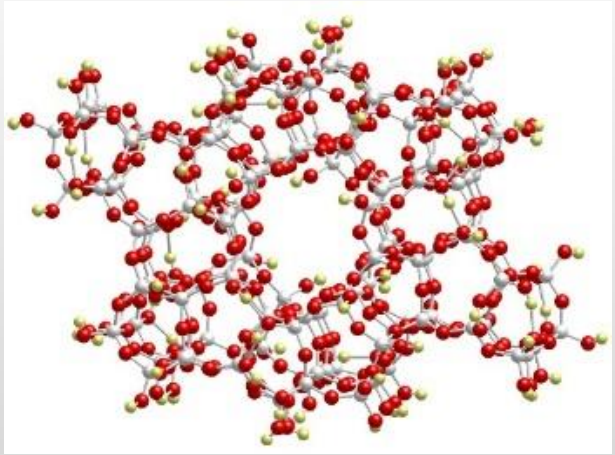
Transition metals



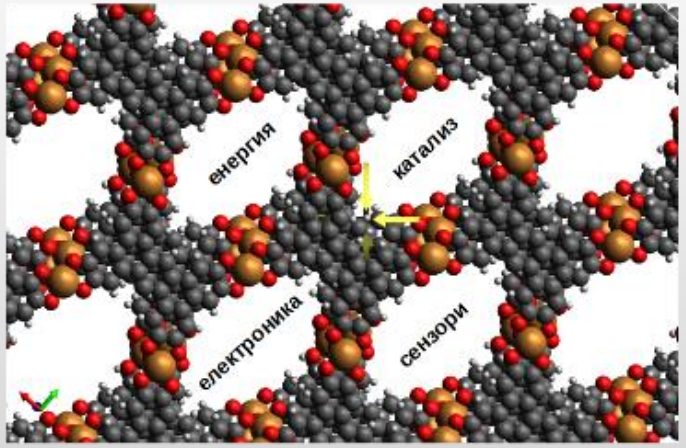


Metal oxides





Zeolites

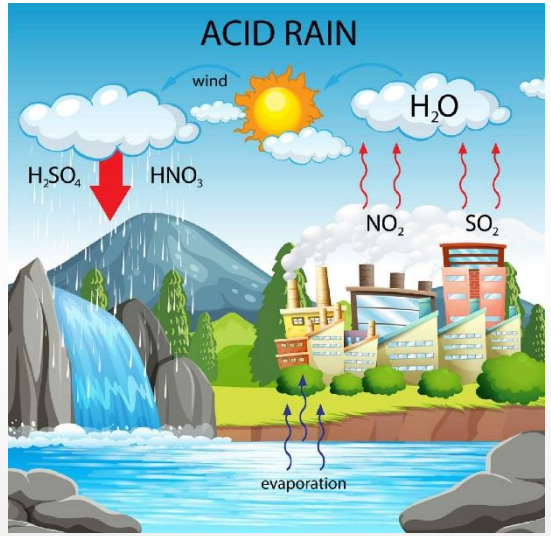


Metal-organic frameworks (MOFs)

NO oxidation to NO_2 on TM/CeO_2

- NO oxidation to NO_2 is critical for environmental catalysis in diesel aftertreatment systems because:

  - NO_2 formation is important in lean NOx reduction
  - NO_2 facilitates ammonia selective catalytic reduction (SCR) (so-called "fast" SCR, with an ideal 1:1 ratio between NO and NO_2)
  - Lean NO*x* storage - NO must first be oxidized to NO_2 to be stored on LN traps materials

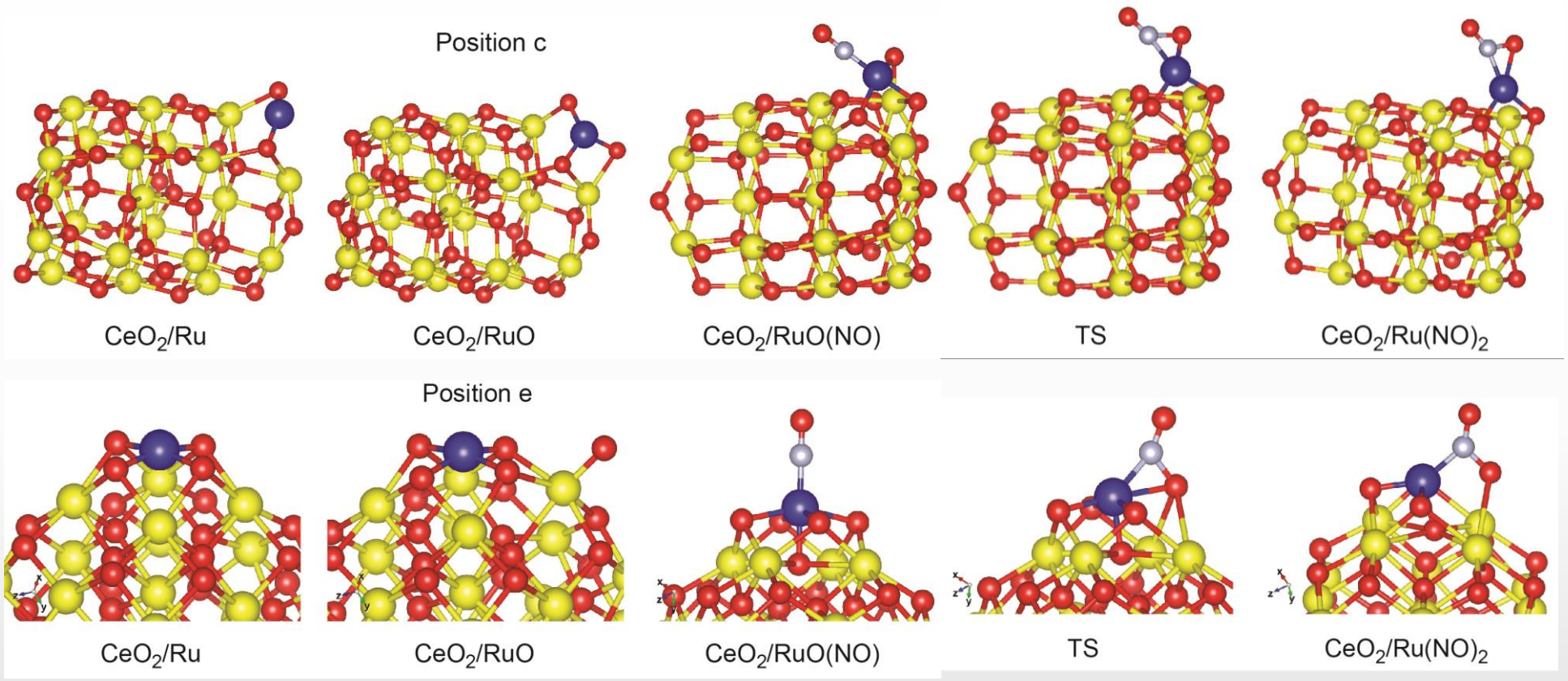


https://www.climateandweather.net/world-weather/acid-rain/

- Best catalysts for NO oxidation typically contain a few wt % percent of expensive Pt and Pd
- Catalyst with atomically dispersed Ru_1O_5 sites on (100) facets of ceria - only 0.1−0.5 wt % of Ru is sufficient to achieve high catalytic activity

J. Am. Chem. Soc., **2023**, 145, 9, 5029–5040

NO oxidation on $Rh^{II}O/Ce_{21}O_{42}$



- The rate-limiting step is NO oxidation - $\Delta G^{\#}_{623}$ are 154 and 200 kJ/mol, respectively, on c-1O and e-1O sites
- The former barrier seems to be operative at 623 K, as the calculated kinetic constant is 1.58 s^{-1} which corresponds to a half-life T½ of ~0.44 sec

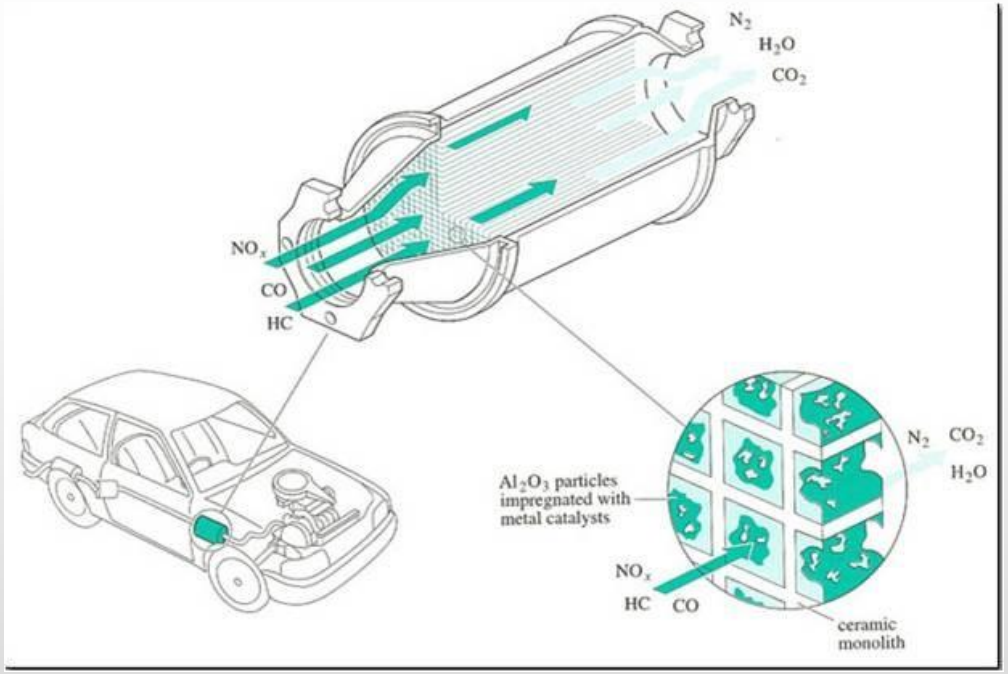
J. Am. Chem. Soc., **2023**, 145, 9, 5029–5040

CO oxidation on Pt/CeO_2

- CO oxidation to CO_2 is a key process in various industrial reactions:

- Conversion of automotive exhaust gases into harmless ones
- Water−gas shift reaction (WGSR)
- Preferential CO oxidation in the presence of hydrogen (PROX)
- Reforming of alcohols etc.

- Pt/CeO_2 - high catalytic activity for CO oxidation under various reaction conditions



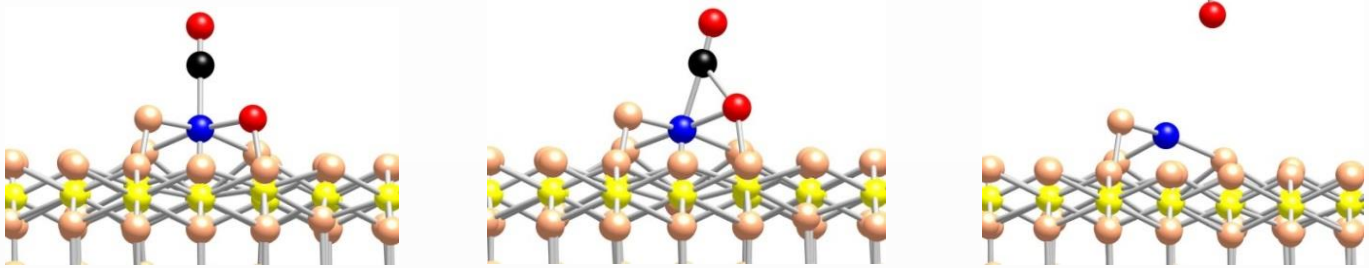
https://www.linkedin.com/pulse/emission-control-gasolinepetrol-engine-three-way-catalytic-tharad

ACS Catalysis, **2023**, *13*, 8, 5358–5374

CO oxidation on mononuclear $Pt^{4+}(O)_2$ species

E_a= 35 kJ/mol
E_{FS-IS} = -112 kJ/mol

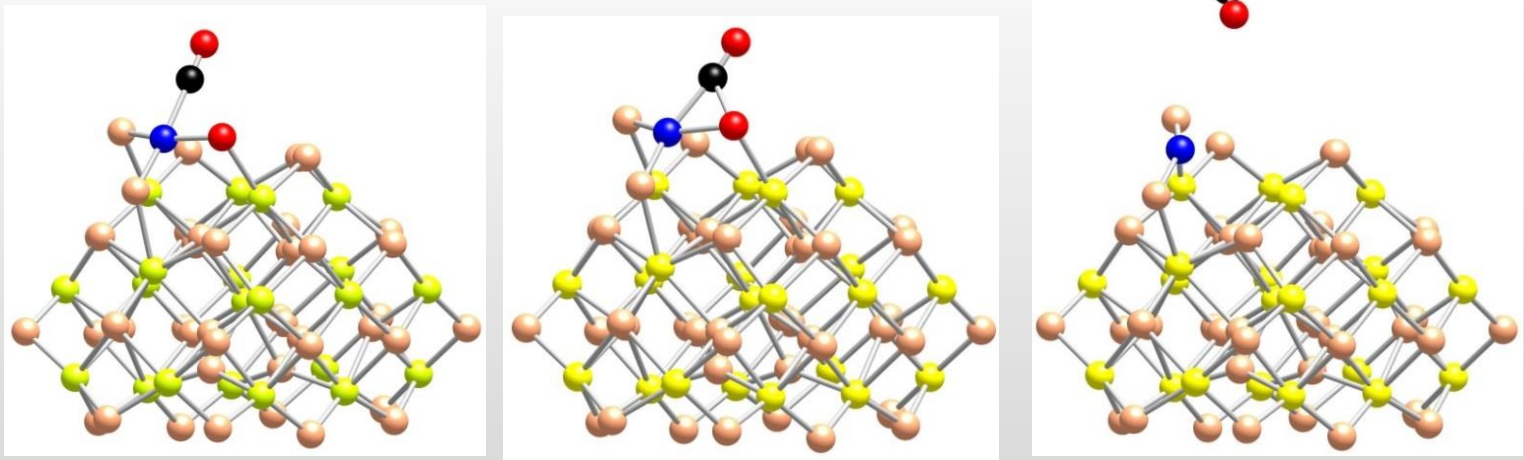
CeO_2 (111)



IS $Pt^{4+}(O)_2(CO)$ **TS** **FS** $Pt^{2+}(O)$ + CO_2

E_a= 22 kJ/mol
E_{FS-IS} = -105 kJ/mol

$Ce_{21}O_{42}$ nanoparticle

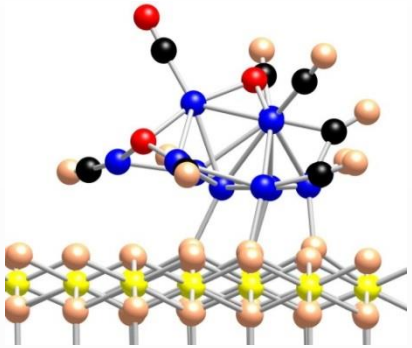


ACS Catalysis, **2023**, *13*, 8, 5358–5374

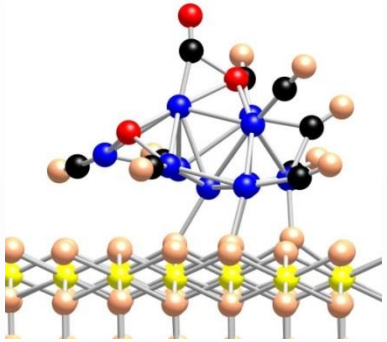
CO oxidation on Pt_8 clusters

E_a= 104 kJ/mol
E_{FS-IS} = -50 kJ/mol

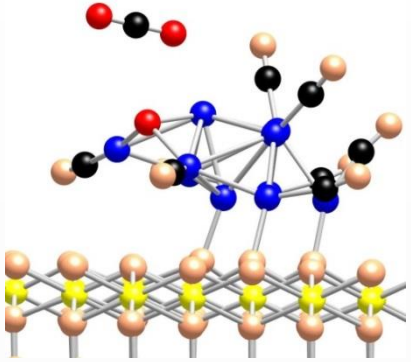
CeO_2 (111)



IS $Pt_{10}(CO)_9(O)_2$



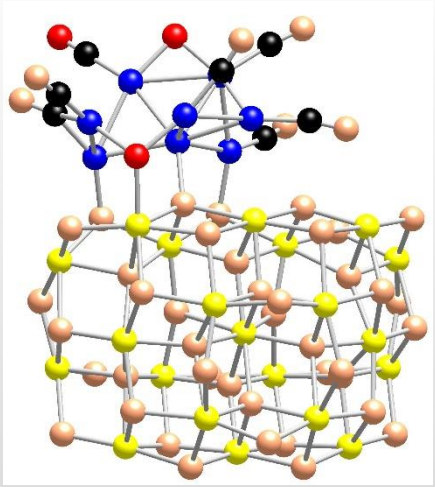
TS



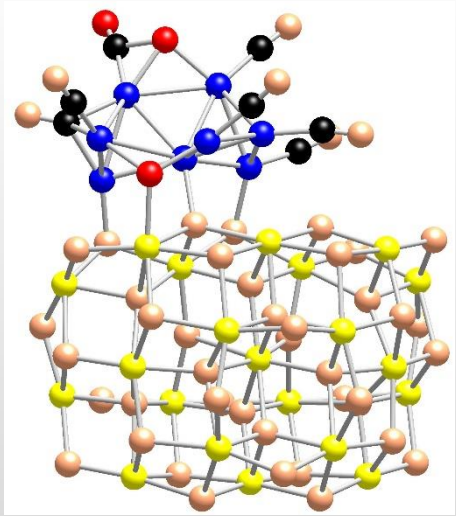
FS $Pt_{10}(CO)_8(O)+CO_2$

E_a= 70 kJ/mol
E_{FS-IS} = -122 kJ/mol

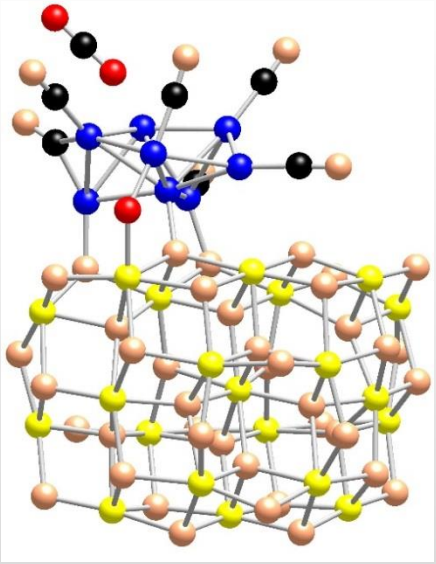
$Ce_{21}O_{42}$ nanoparticle



IS $Pt_8(CO)_7(O)_2$



TS

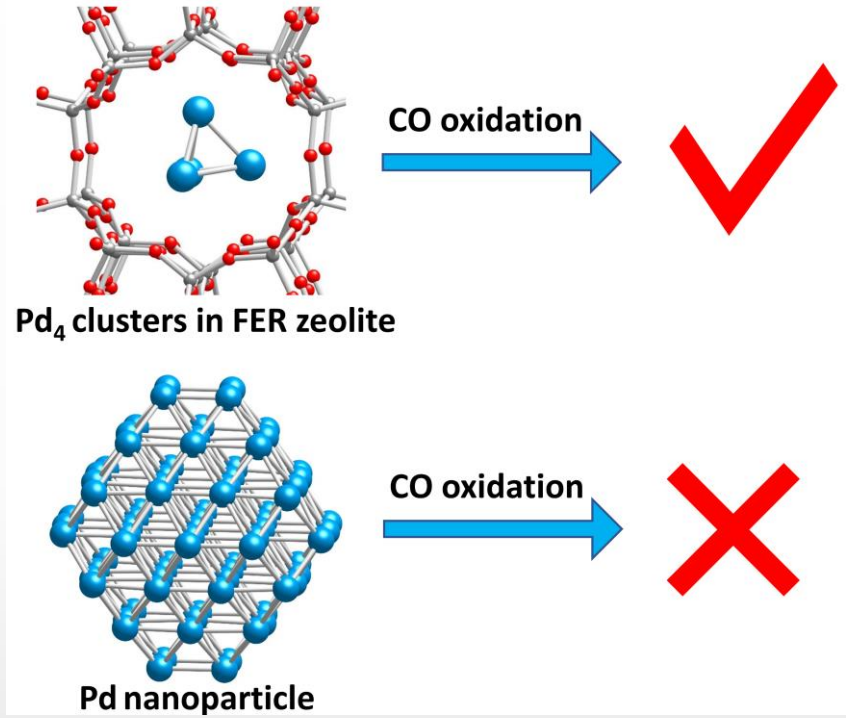


FS $Pt_8(CO)_6(O)+CO_2$

ACS Catalysis, **2023**, *13*, 8, 5358–5374

CO oxidation on Pd catalysts

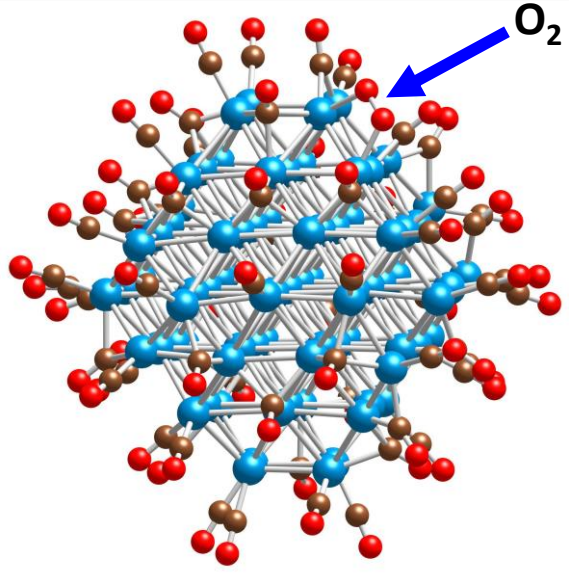
- Low catalytic activity of Pd nanoparticles – catalytic sites blocked by CO
- High catalytic activity of Pd_4 clusters supported in FER zeolite
- O_2 adsorption seems to be the crucial step of the process



J. Am. Chem. Soc., **2023**, *145*, 50, 27493–27499

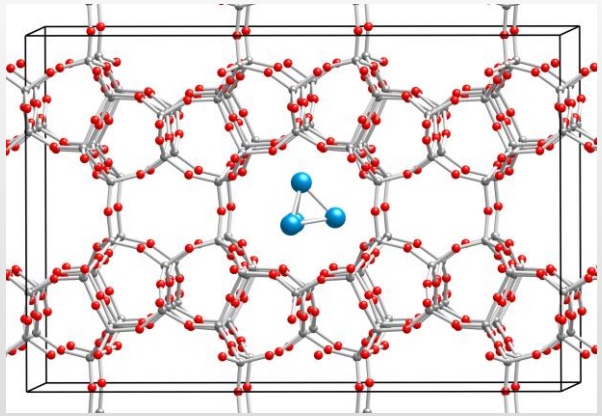
CO and O_2 adsorption on Pd_{79} NP and Pd_4/FER

- Higher flexibility of Pd_4 cluster upon CO adsorption than significantly larger Pd_{79}
- O_2 binds stronger to the Pd_4 cluster than to the Pd_{79} NP
- Significant activation of O-O bond on Pd_4 cluster

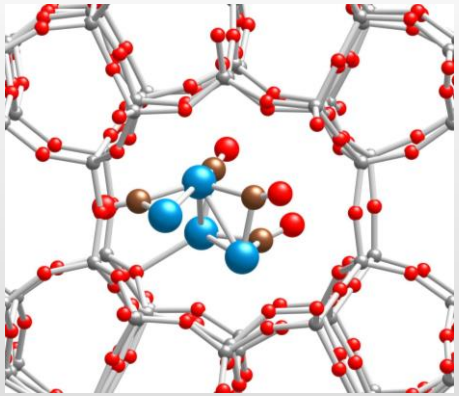


$Pd_{79}(O_2)(CO)_{60}$
$BE(O_2)$ = -120 kJ/mol
Δ(O-O) = 7.6 pm

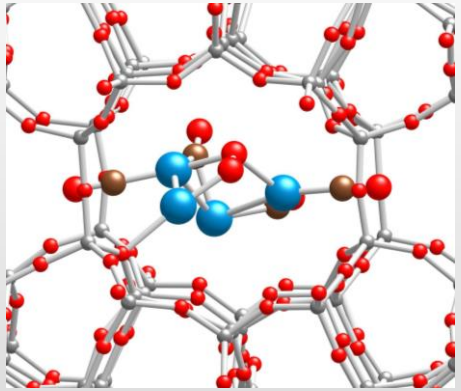
J. Am. Chem. Soc., **2023**, 145, 50, 27493–27499



Pd_4/FER

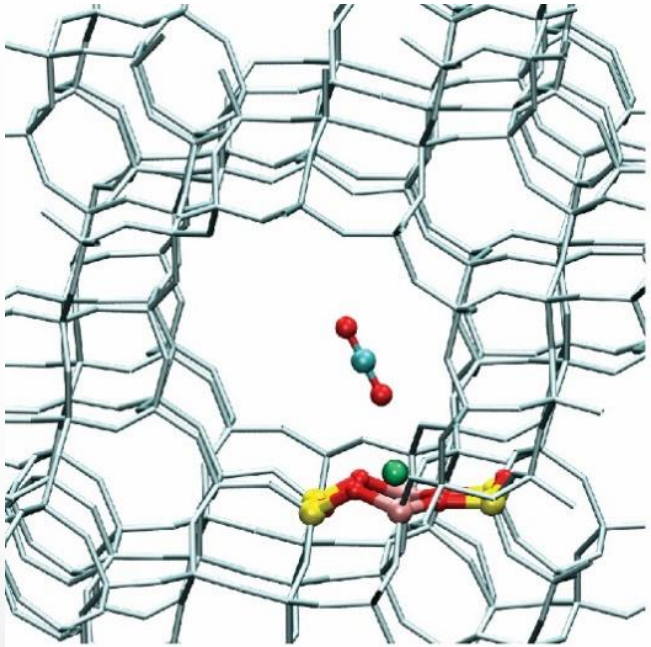


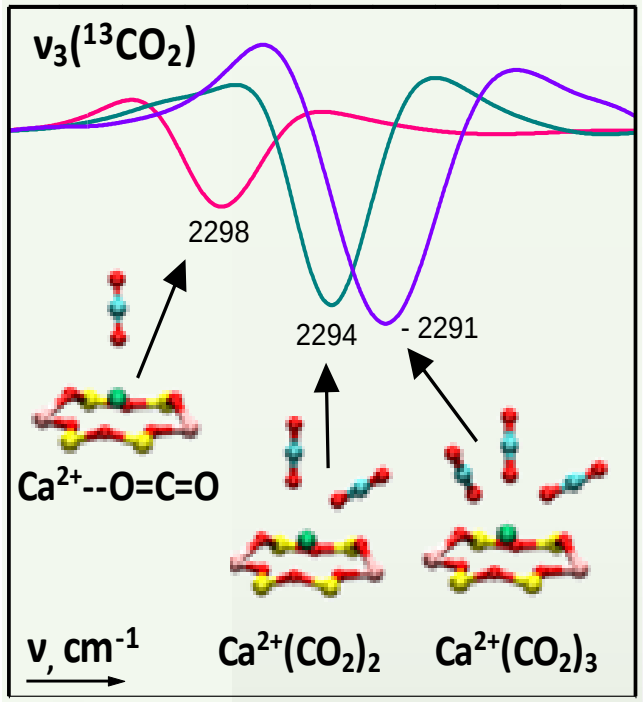
$Pd_4(CO)_4$/FER

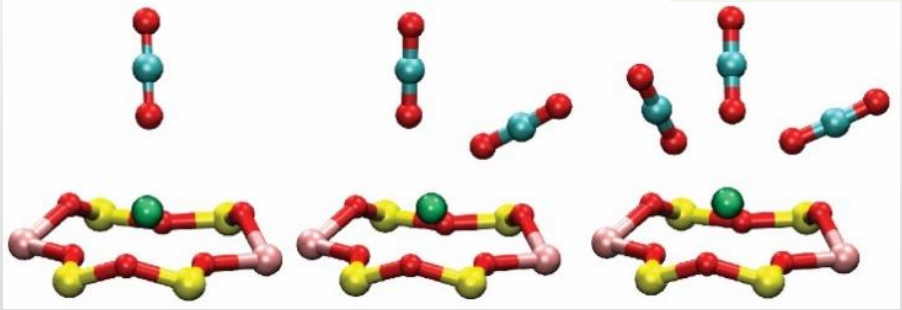


$Pd_4(CO)_4(O_2)$/FER
$BE(O_2)$=-142 kJ/mol
Δ(O-O) = 19.8 pm

Zeolites – potential CO_2 sorbents





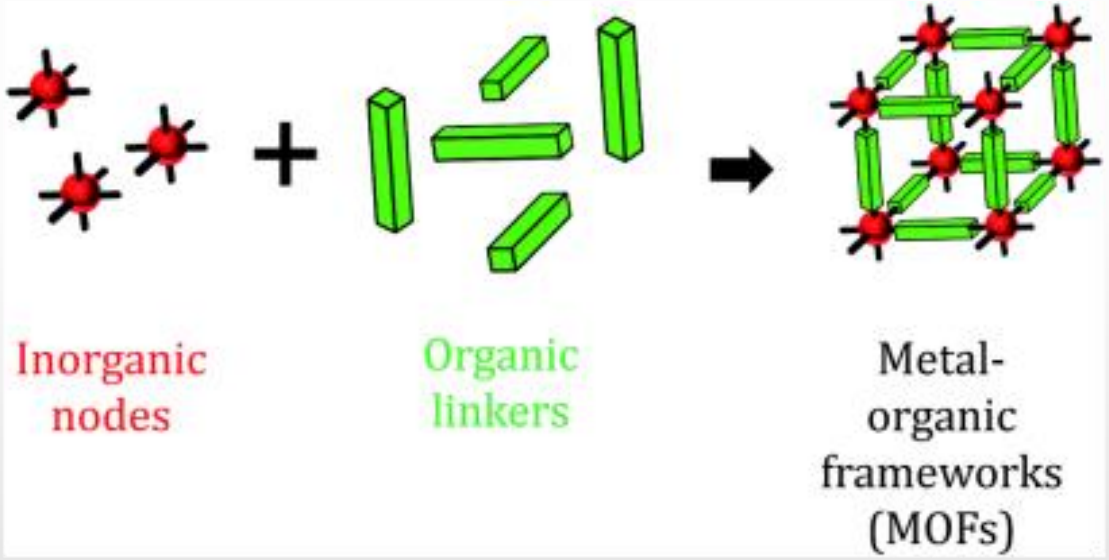


- Crystalline porous aluminosilicates
- 3D structures with crystal lattice: $[SiO_4]$ and $[AlO_4]$
- CaY zeolites possess a high CO_2 adsorption capacity at ambient temperature
- Each Ca^{2+} site can attach two CO_2 molecules at relatively low partial pressure and has the reserve potential to bind an additional molecule when the equilibrium pressure increases

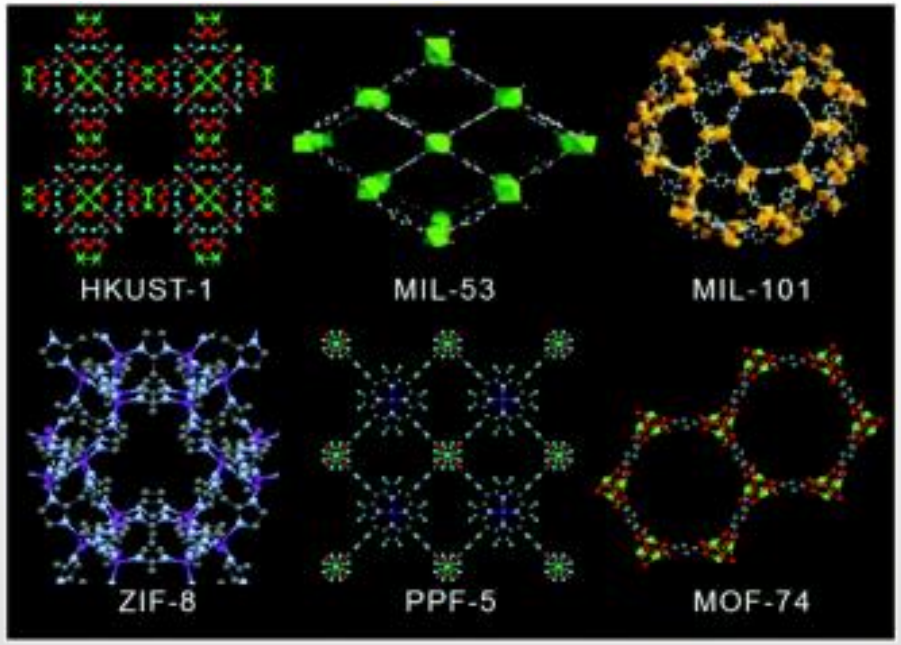
J. Phys. Chem. Lett., **2023**, *14*, 6, 1564–1569

Metal-organic frameworks (MOFs)

MOFs: Crystalline class of porous materials assembled from inorganic metal nodes and organic linkers



Energy Environ. Sci., 2015,8, 1190-1199



Chem. Soc. Rev., 2014,43, 5994-6010

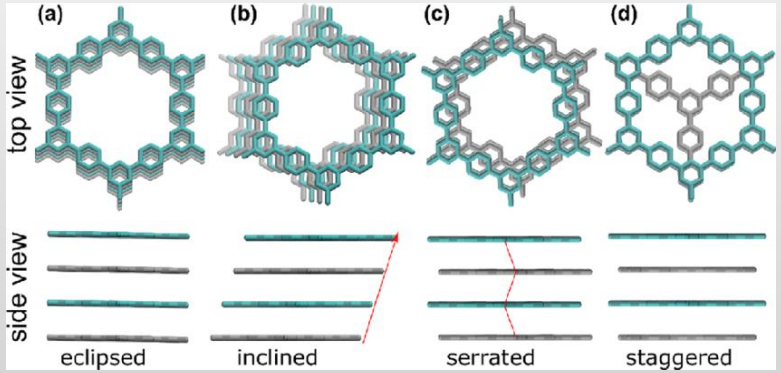
MOFs – properties and applications

- high porosity
- huge inner surface
- crystallinity
- tunability (linker, metal ions, defects)
- deposition as thin films

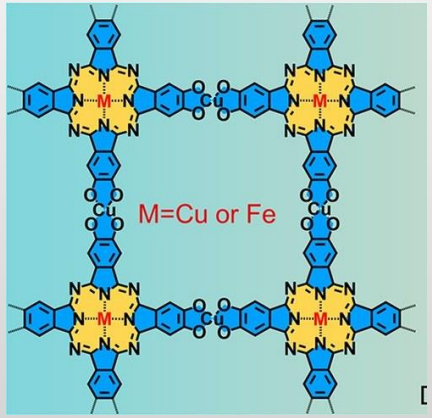
- gas storage & separation
- drug storage & release
- energy storage
- sensors
- structure property relationships
- etc.

2D conjugated metal–organic frameworks (c-MOFs)

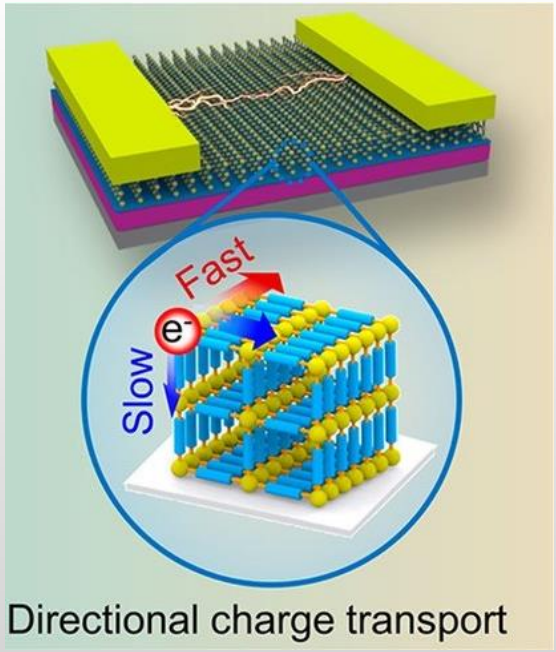
- Highly tailorable, their conductivity, charge carrier mobility and band-gap can be controlled through the appropriate design.
- Two general approaches towards 2D c-MOF design:
  - "**in-plane**" approach (*through the bonds*)
  - "**out-of-plane**" approach (*through the space*)



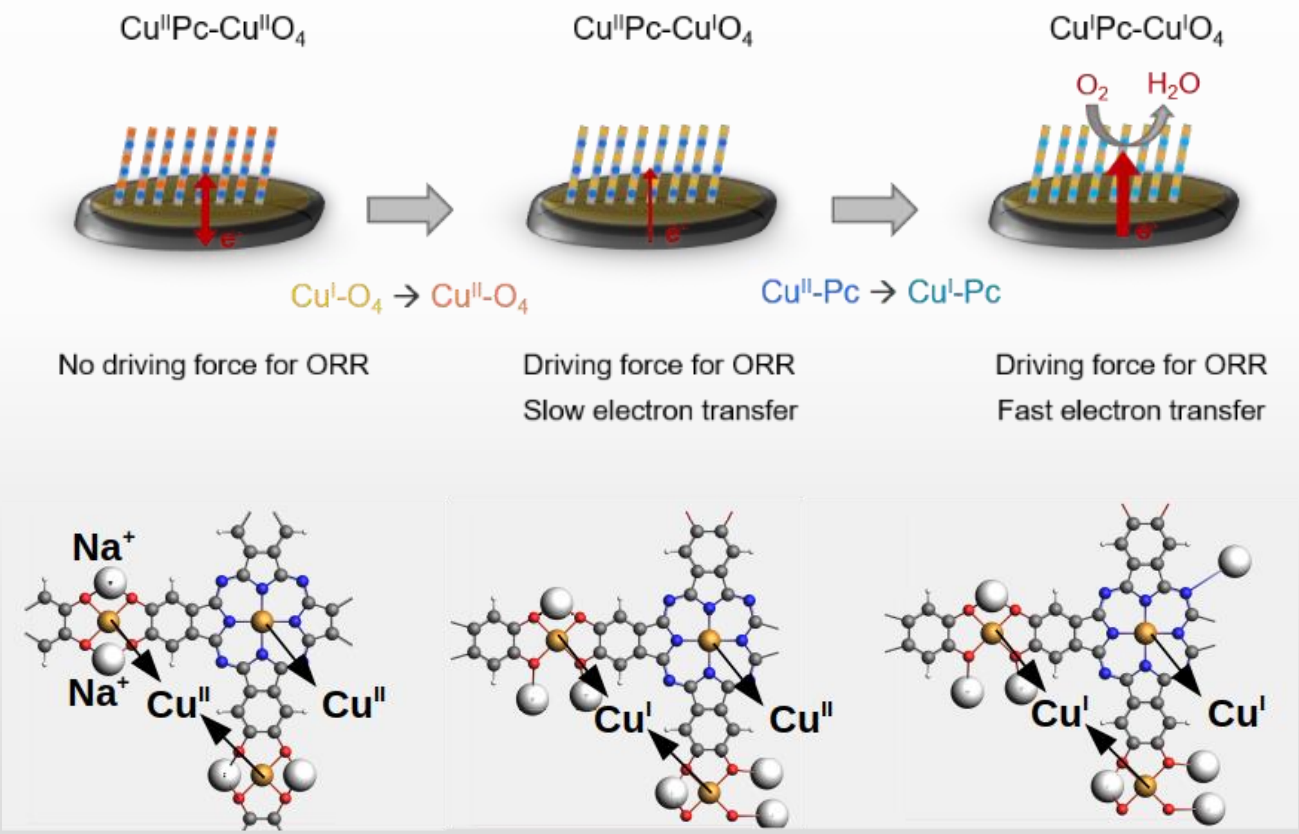
ACS Appl. Nano Mater. **2022**, *5*, 10, 14377–14387



J. Am. Chem. Soc. **2021**, *143*, 34, 13624–13632

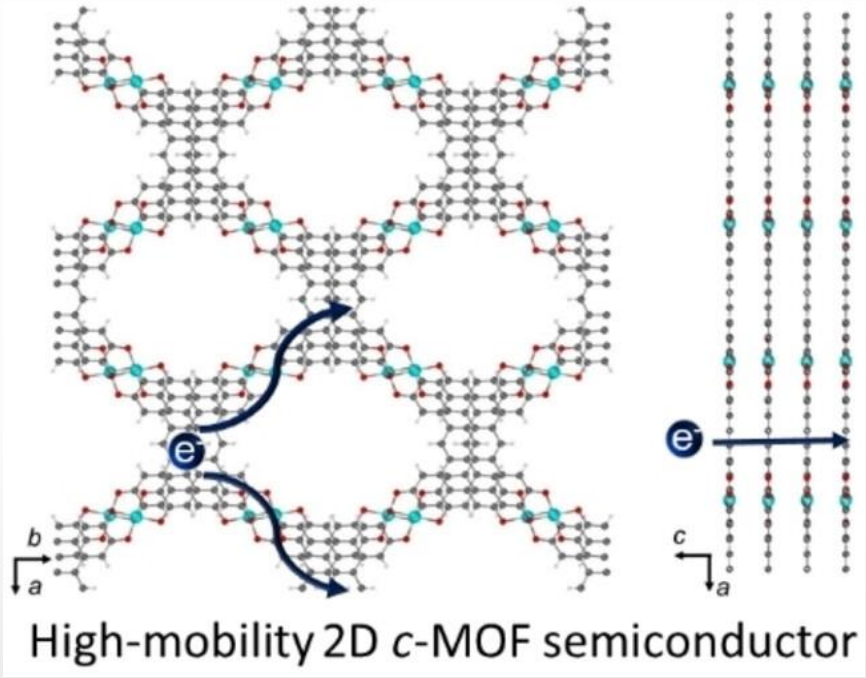


Oxidation State Dependent Conjugation Controls Electrocatalytic Activity in a Two-Dimensional Di-Copper Metal–Organic Framework



J. Phys. Chem. C, **2023**, *127*, 15, 7299–7307

Near IR Bandgap Semiconducting 2D Conjugated Metal-Organic Framework with Rhombic Lattice and High Mobility



DFT: the large aromatic core of the ligands leads to improved π-π interactions normal to the layers, which contributes to strong band dispersion close to the Fermi level and dominates the overall conductivity.

Angew. Chem. Int. Ed., **2023**, *62*, e202300186

Research achievements in 2023

- The group published 21 publications in 2023, which exceeds the number of publications planned for 2024 (16) and 2025 (19)
- The total impact factor (IF) of these papers is 206.9 (average IF of 9.94)
- 14 of the publications are in the area of computational heterogeneous catalysis - total IF is 178.8 (average IF of 13.39)
- These studies were published in some of the most prestigious scientific journals in the areas of:
  - Chemistry: *Angew. Chem. Int. Ed.*; *J. Am. Chem. Soc.*
  - Catalysis: *ACS Catalysis*
  - Materials: *Nat. Mater.; Micropor. Mesopor. Mater.; Chem. Mater.*
  - Theoretical and physical chemistry: *J. Phys. Chem. Lett.; J. Phys. Chem. C*

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SUMMIT

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THANK YOU!