COMPUTATIONAL CHEMISTRY DAY 2025

Faculty of Chemistry and Technology, Split
Department of Mathematics and Physics

TRANSLATING INSIGHTS FROM GAS PHASE CATALYSTS INTO SOLID STATE MATERIALS FOR SUSTAINABLE FUTURE

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J. Heyrovský Institute of Physical Chemistry

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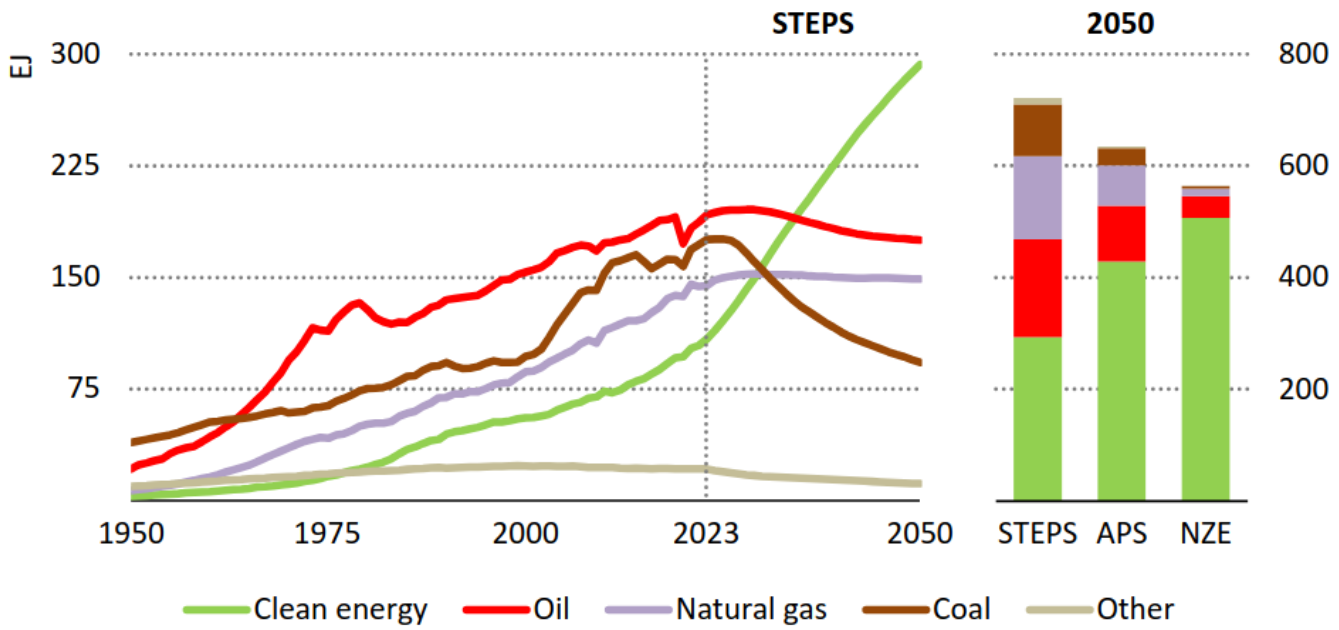
THE UNIVERSITY OF MELBOURNE

7.6.2025.

RESEARCH CONTEXT

Global energy mix by scenario to 2050



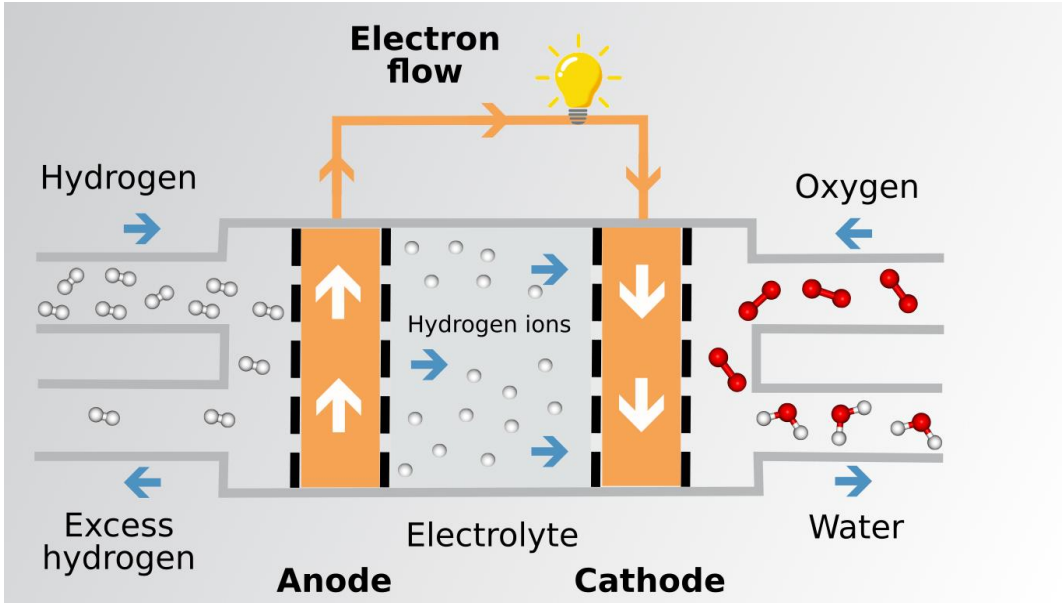
World Energy Outlook, *IEA*, 2024.

- The fossil fuels share in the global energy use is around **80%**.
- Energy demand can be met by renewables in the power and end-use sectors, low-emissions fuels, including carbon capture, utilization and storage.
- **Materials science:** offering solutions for sustainable reutilization of harmful gases and production of value-added chemicals.

SUSTAINABLE FUTURE

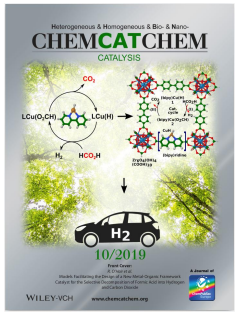
MATERIALS FOR FUEL CELLS

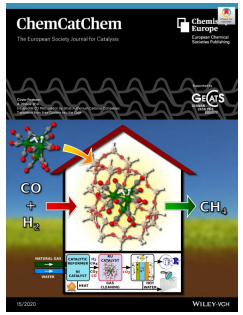
- PEMFCs – clean and promising technology.
- H_2 comes from fossil fuel reforming.
- CO (even at 10-20 ppm) poisons the Pt-anode.



Adapted from *Mater. Sci. Eng.* IOP Publishing, 2018.

Increasing efficiency through hydrogen production and elimination of carbon monoxide.

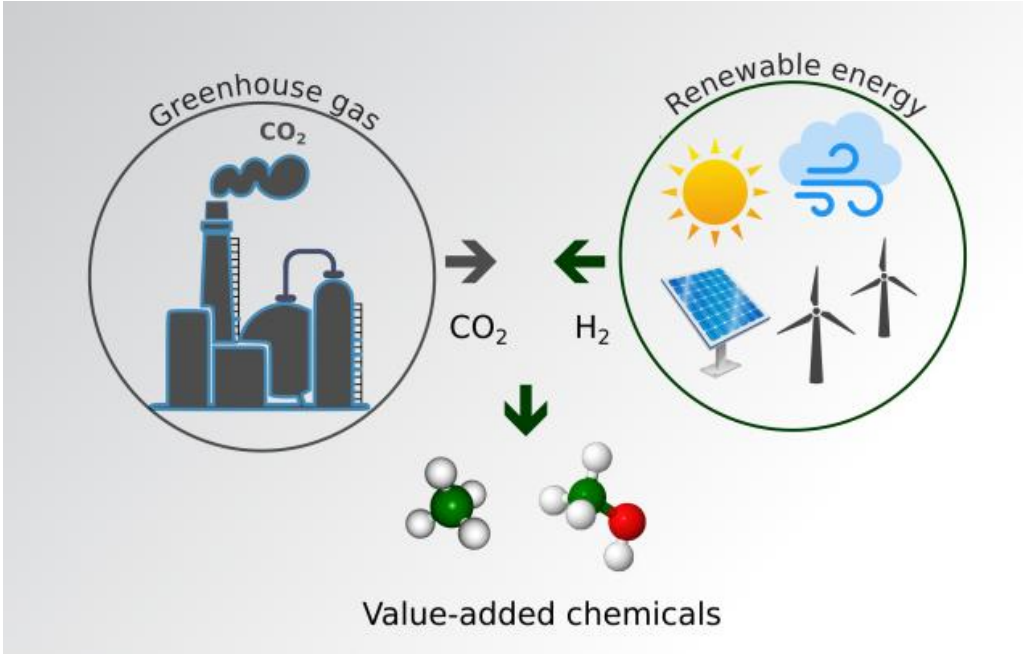




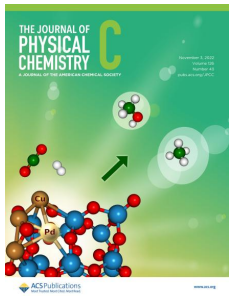
SUSTAINABLE FUTURE

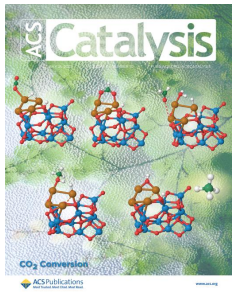
CO_2 REMOVAL AND UTILIZATION

- CO_2 is highly abundant greenhouse gas.
- CO_2 hydrogenation: production of energy rich molecules (like methane and methanol).
- Development of efficient and cheap catalysts for CO_2 conversion.



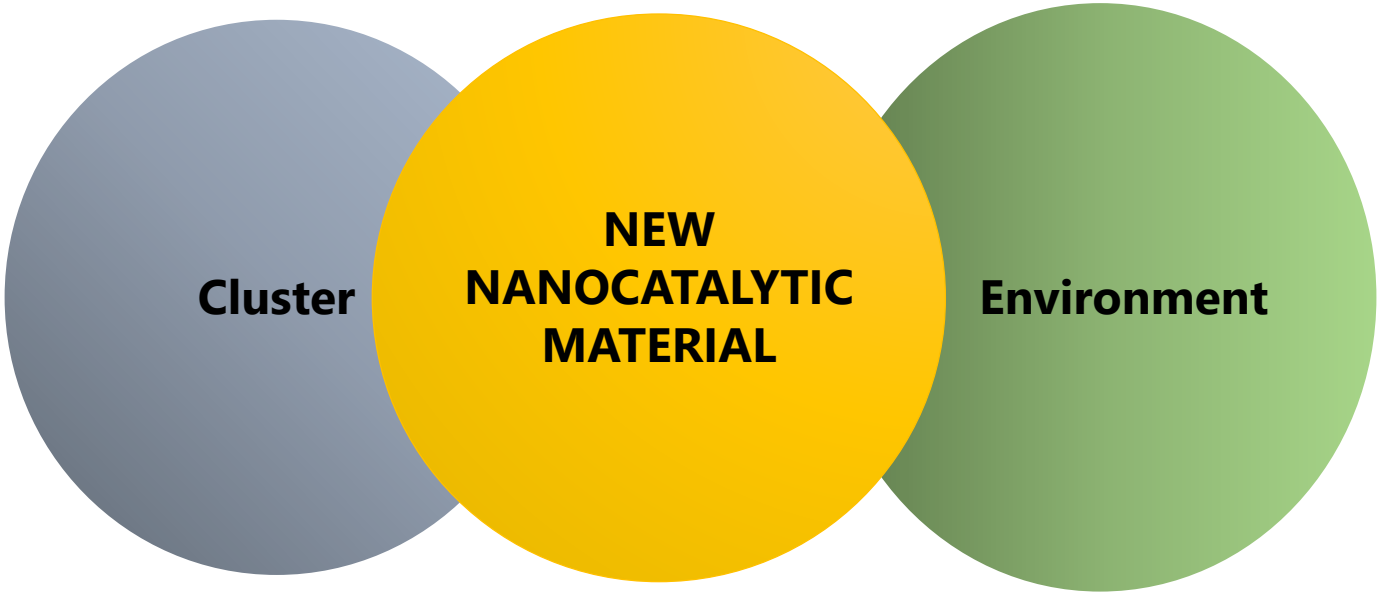
Elimination of the greenhouse gas and its conversion into methane and methanol.





"We seem to be forced to the conclusion that we know little or nothing concerning the effect which such aristocracies of atoms exercise on the impinging reactants. … The general problem of activation (of reactants) is of such fundamental importance that every chemist in the world should be keeping it in mind so as to be ready to do his share in the solution."

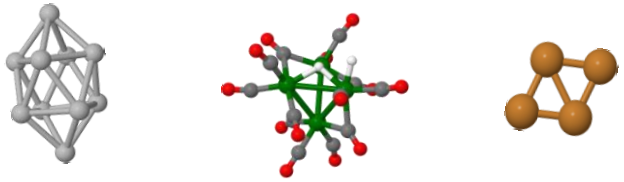
H. S. Taylor, *J. Phys. Chem.* 1926, 30, 145.



NANOCATALYSTS

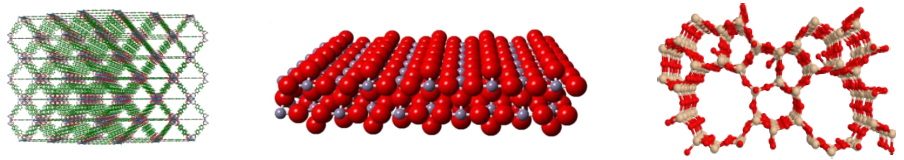
SIZE-SELECTED NANOCLUSTERS

- Quantum size effects.
- Individual active sites.
- Activity and selectivity of the reaction.
- Synergistic effect of bimetallic clusters.
- A higher number of under-coordinated atoms (enhanced activity).



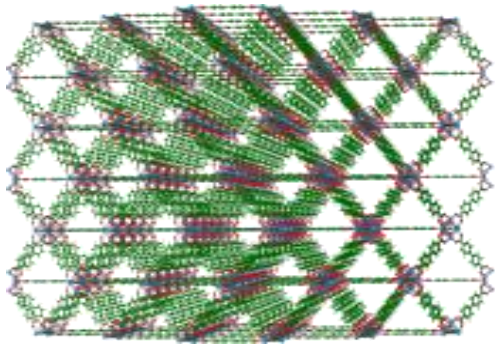
ENVIRONMENT

- Possible influence on the character of the cluster via charge transfer.
- Influence on cluster mobility.
- Protection, stabilization.
- (In)activation of the catalyst.
- Synergistic effects.



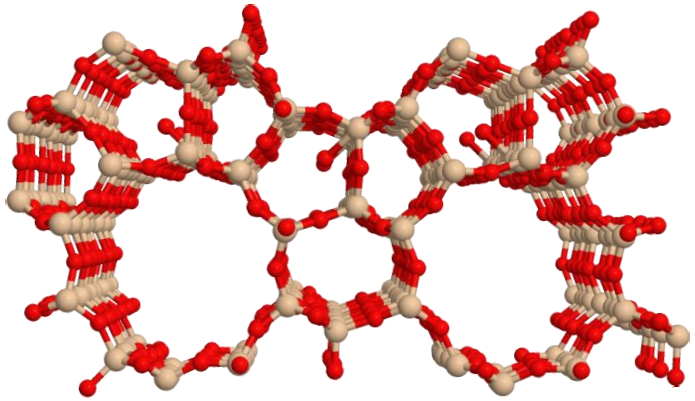
METAL-ORGANIC FRAMEWORK (MOF)

- Versatile in size and composition.
- Large surface area.
- Accessible to substrates, easy removal of products.
- Different catalytic sites.



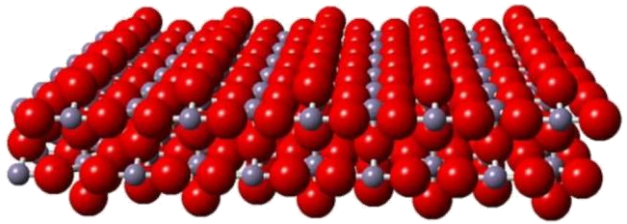
ZEOLITE

- Microporous.
- Large surface area.
- Highly robust.
- High thermochemical stability.
- Cheap production.



OTHER METAL-OXIDE SURFACES

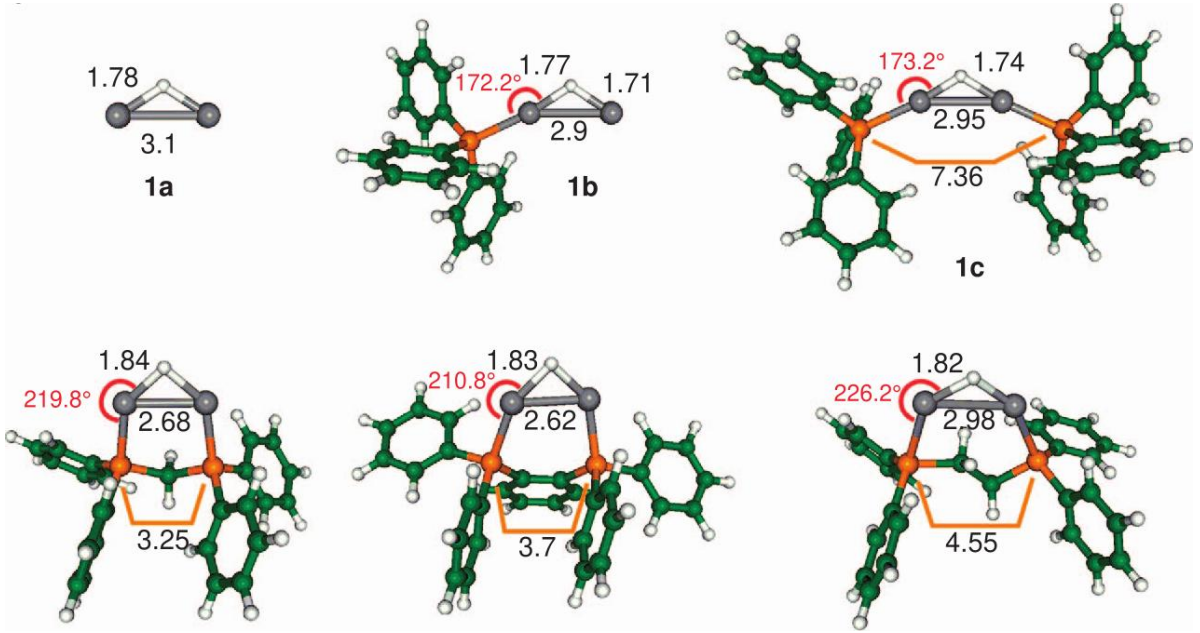
- Facile to undergo reconstructions.
- Catalytically active.
- Their morphology can play important role in activity.



1. CATALYSTS FOR H_2 PRODUCTION

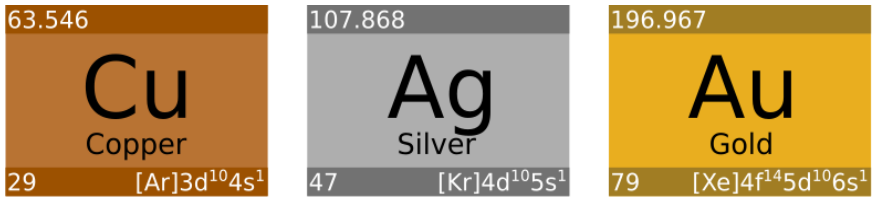
METAL HYDRIDES

- Coinage metal hydrides are usually monovalent.
- d-electrons remain energetically accessible which is necessary for bonding and reactivity.
- Unique reactivity and high potential for catalytic transformations.



Nat. Commun. 2016; 7(1):1-8

Bonačić-Koutecký group



Ligands have a key role in reshaping the scaffold of the cluster, activating its reactivity towards a substrate.

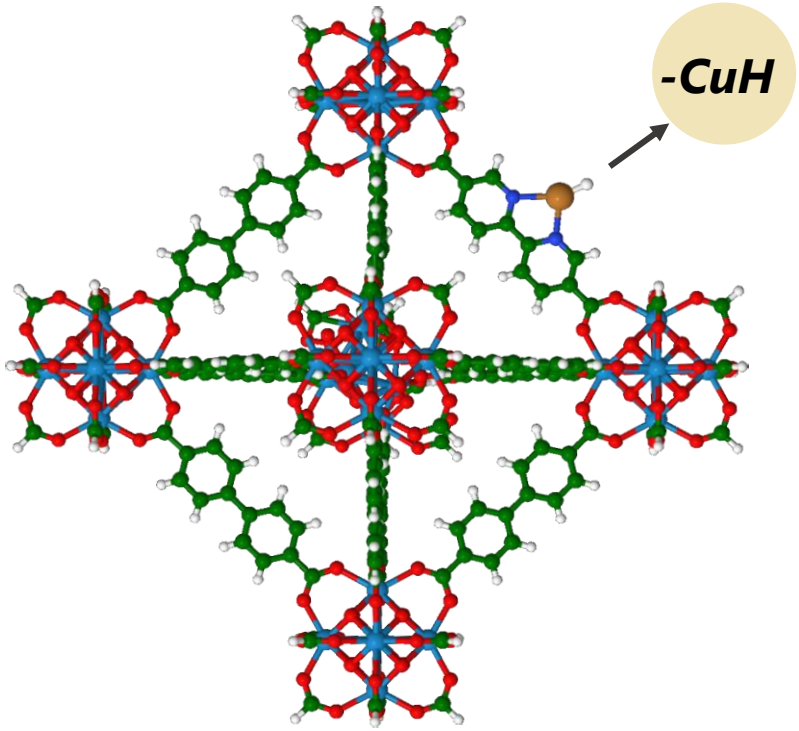
DESIGN OF MOF-BASED CATALYST

Integration of reactive center into the MOF

THE UNIVERSITY OF MELBOURNE
O'Hair group

GOAL

Design of new heterogeneous catalyst for *in situ* H_2 generation and storage.



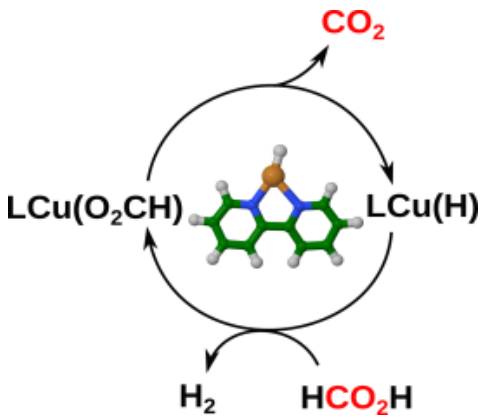
UiO-67

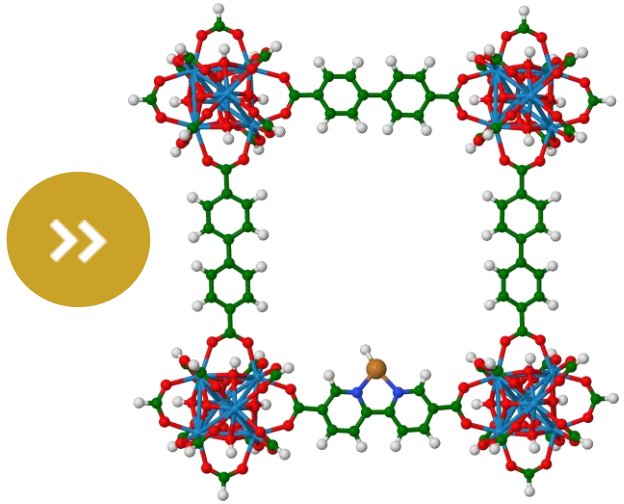
REACTION

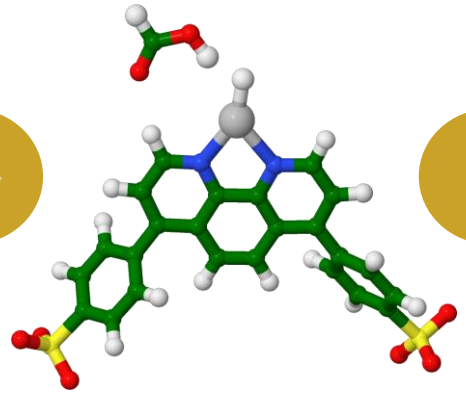
Selective decarboxylation of formic acid proceeds in two steps:

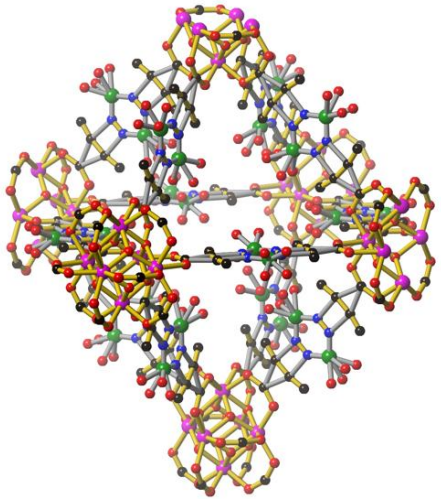
i) liberation of H_2
ii) CO_2 extrusion.

Transferring the concept from gas phase into the MOF









Theoretical modeling of reaction on the gas phase models.

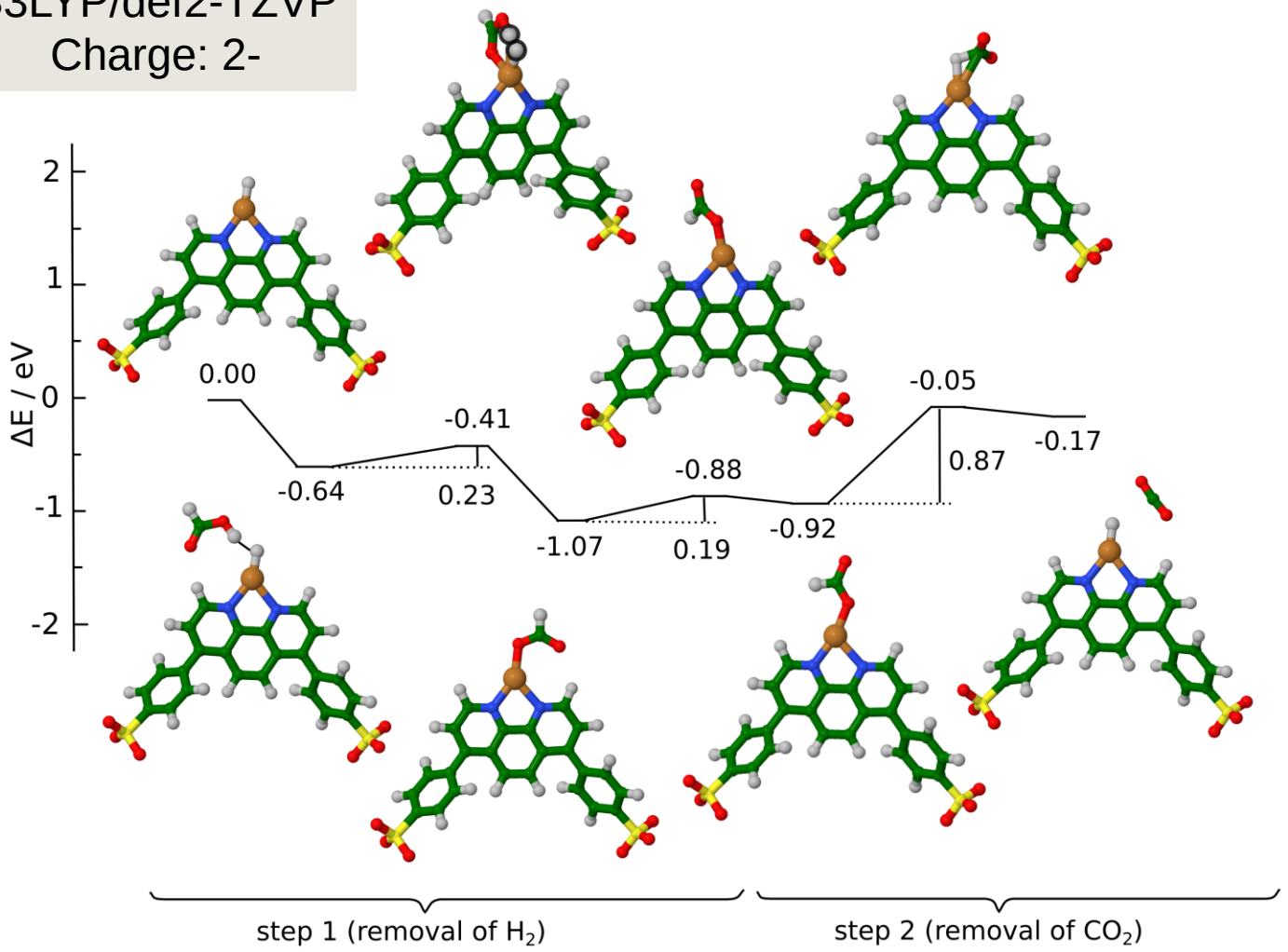
Modeling integration of the reactive center into the MOF.

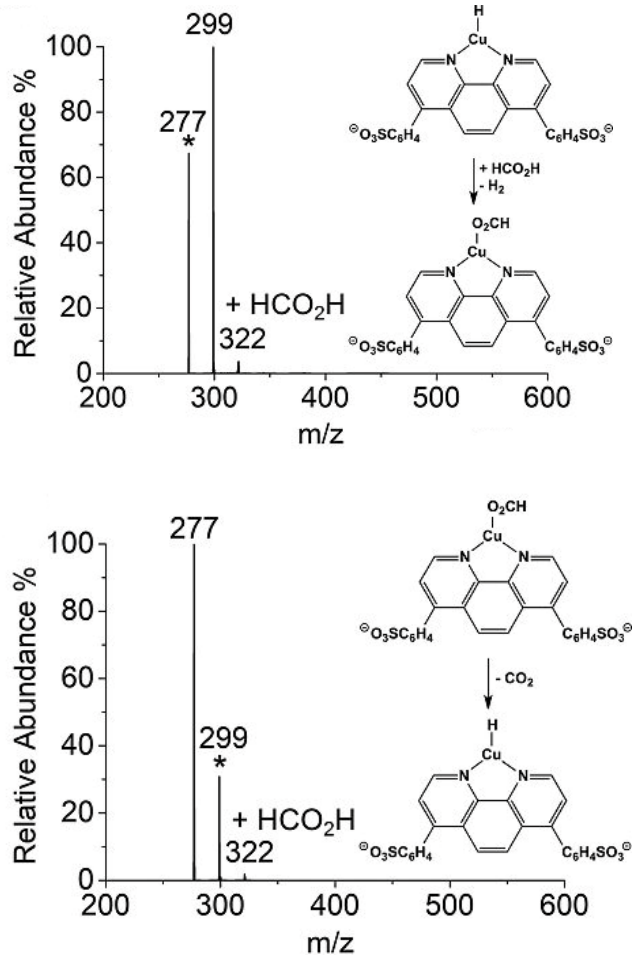
Examining other potential metal centers.

Experimental preparation prof. R. O'Hair, University of Melbourne

Experimental (charged) catalyst model

B3LYP/def2-TZVP
Charge: 2-

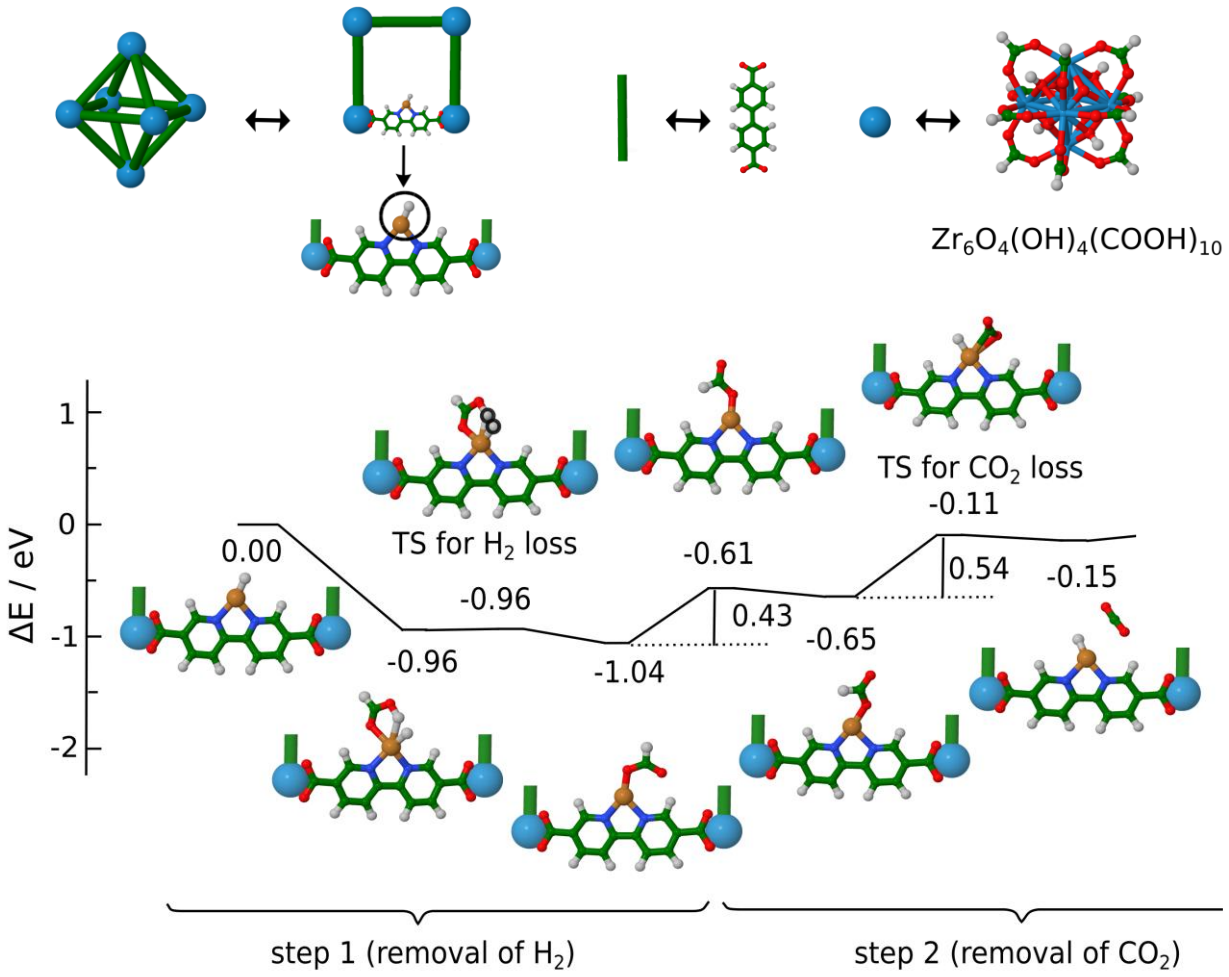


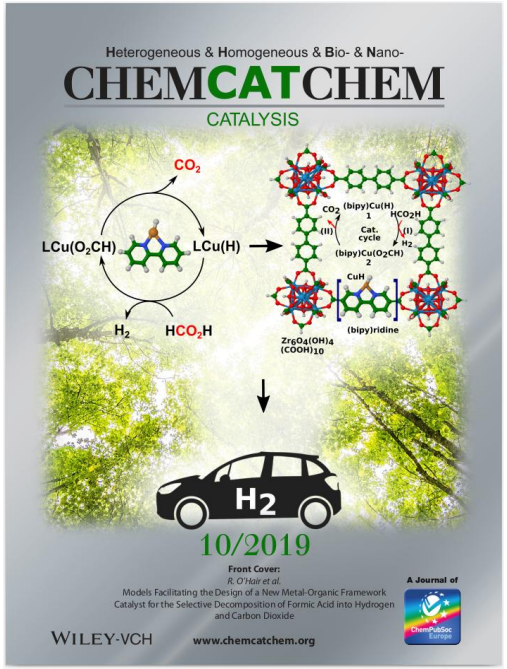


Mass spectra confirms products from theoretical calculations.

MOF UiO67-bypdc square catalyst model

PBE/def2-SVP/W06





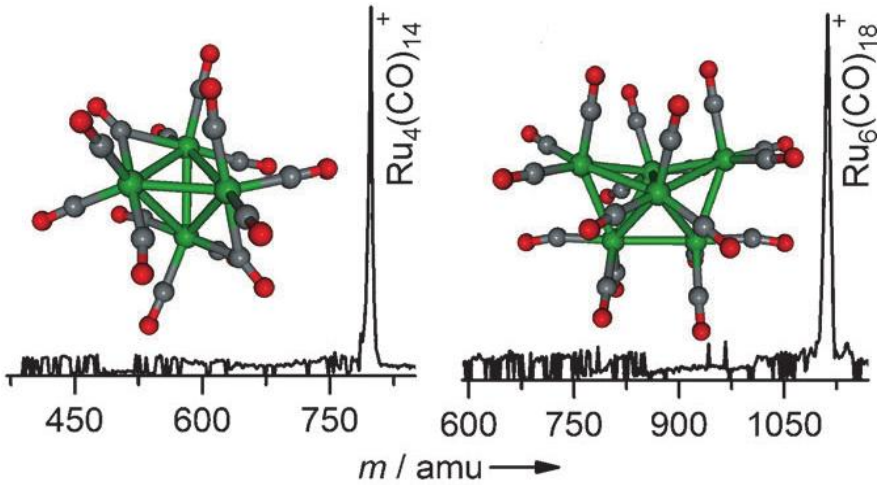
ChemCatChem 2019; 11(10):2443-8.

Illustration of how the simple models contribute to design of new catalytic materials.

2. CATALYSTS FOR CO REMOVAL

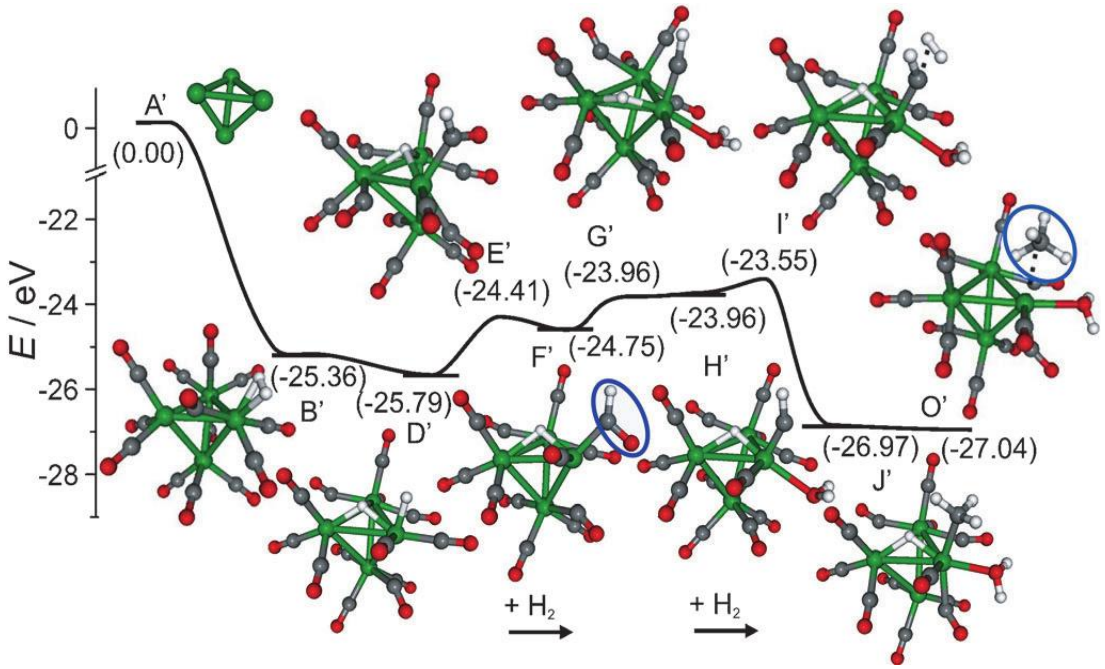
Origin of activity and selectivity of Ru-based catalysts :

- the high reactivity towards CO/inertness towards CO_2;
- the facilitation of H_2 co-adsorption and dissociation;
- low coordinated Ru-atoms are sites for H_2 dissociation.



Angew. Chem., Int. Ed. Engl. 2014; 53(21): 5467-71.

Bonačić-Koutecký group



Angew. Chem., Int. Ed. Engl. 2014; 53(21): 5467-71.

Catalyst for CO methanation - a strategy for purification of the fuel cell feed gas.

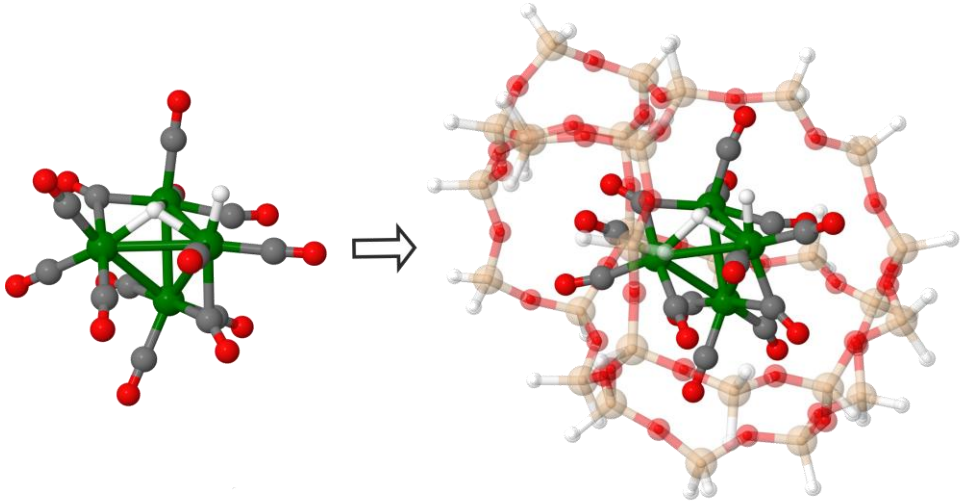
DESIGN OF ZEOLITE-BASED CATALYST

Translation of the free cluster into the cage

Thorsten group

GOAL

Improvement of the feed gas quality by the CO removal in the context of the future applications of fuel cells.

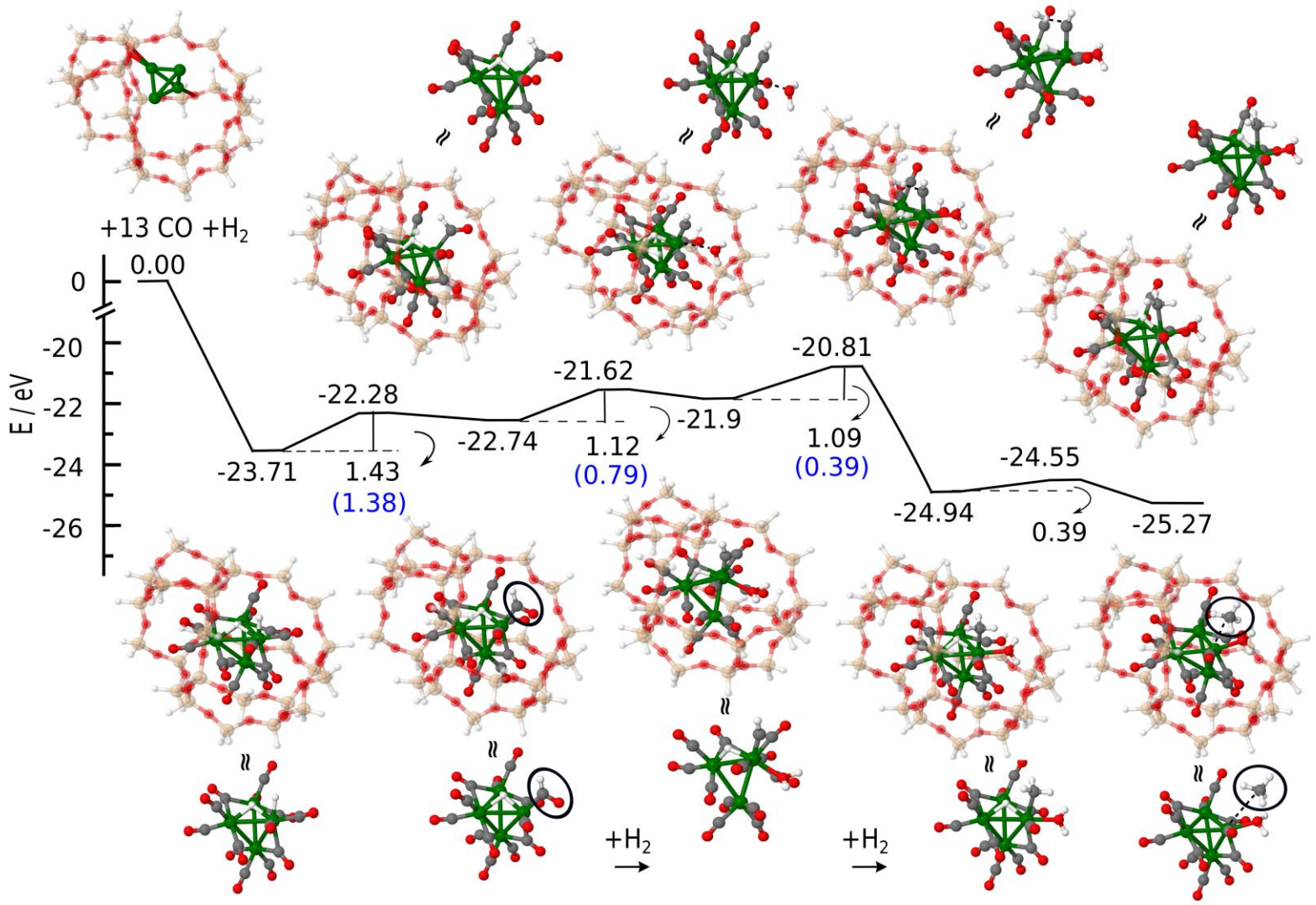


$Ru_4(CO)_{13}H_2^+$ ZSM-5

REACTION

CO methanation mediated by ligated Ru-cluster inside the framework of the zeolite.

CO methanation on zeolite-based catalyst



B3LYP/def2-TZVP
GD3 dispersion

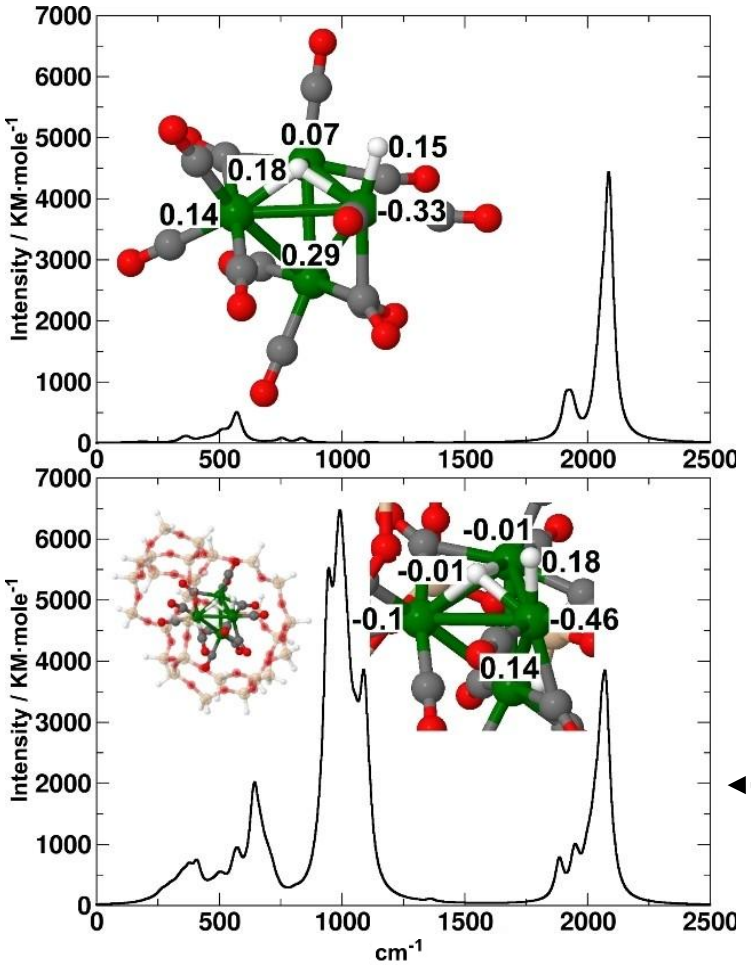
Significant influence of dispersion.

	ΔE[eV]	E_a	Imaginary freq. [cm^{-1}]
TS1	-22.28	1.42	-746.05
TS2	-21.62	1.12	-107.92
TS3	-20.81	1.09	-319.37
TS4	-24.55	0.39	-865.03

Barriers similar to the gas phase.

GAS PHASE

ZEOLITE

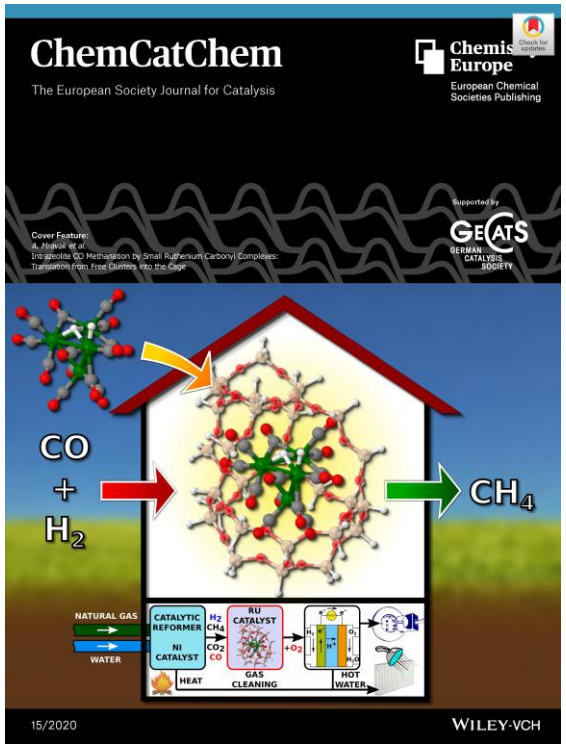


DFT calculated IR spectra

Mulliken charge analysis: small electron transfer to the metal cluster core.

The band centers of CO ligands shifts only for 10 cm^{-1} for the intrazeolite anchored complex.

The reactive center is hardly affected by the zeolite environment.

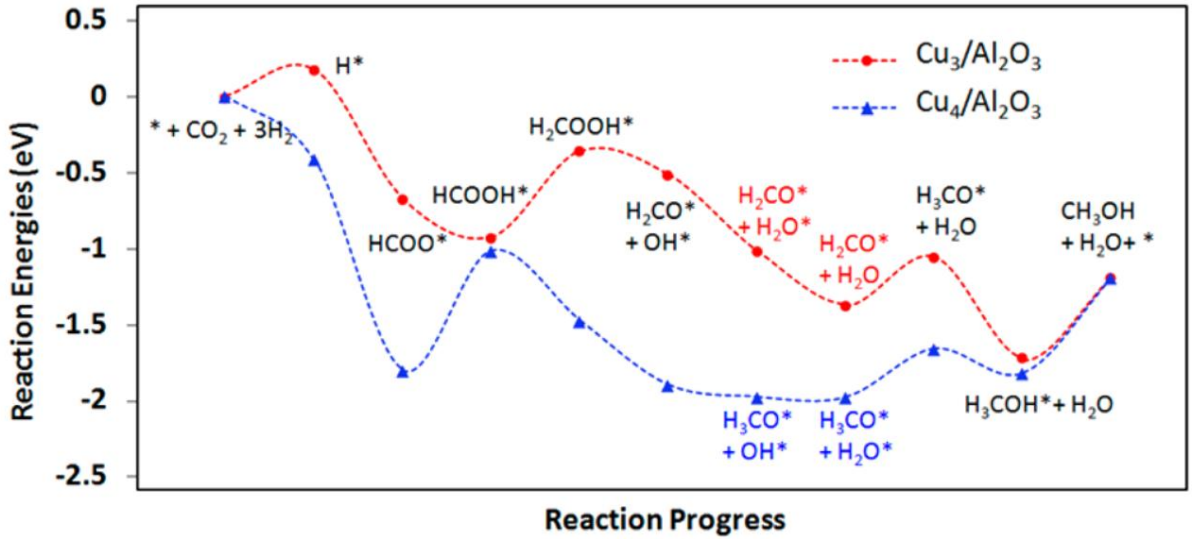


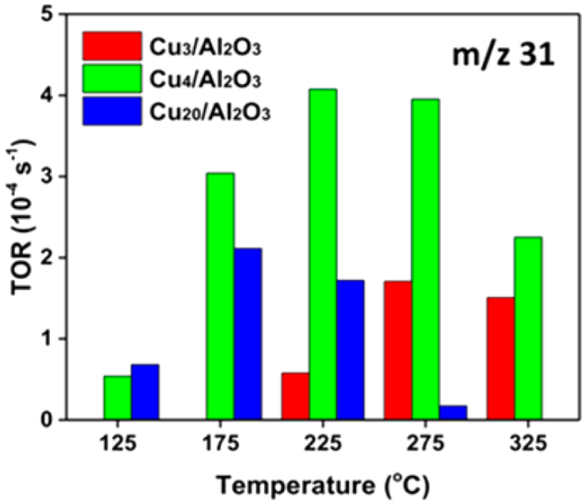
ChemCatChem 2020; 12(15): 3857-62.

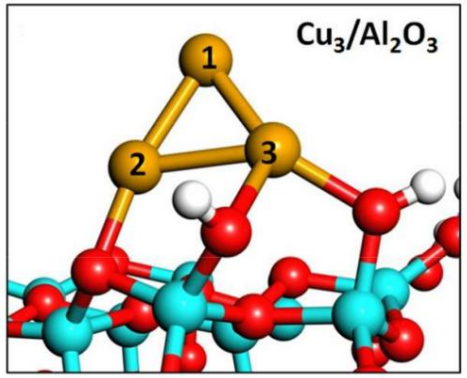
CATALYSTS FOR CO_2 CONVERSION

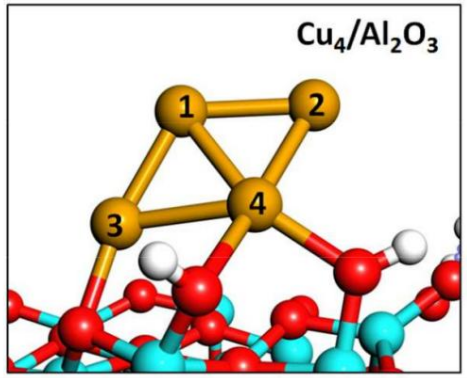
- Size-selected Cu_4 clusters are the most active low-pressure catalyst for catalytic CO_2 conversion to CH_3OH.
  JACS. 2015; 137(27): 8676-9.

- The activity of Cu-clusters is determined by the cluster size and its charge state.









Removal of single atom changes the rate of CH_3OH production!

Vajda group

J. Phys. Chem. C. 2017; 121(19): 10406-12.

DESIGN OF SUPPORTED METAL CLUSTERS

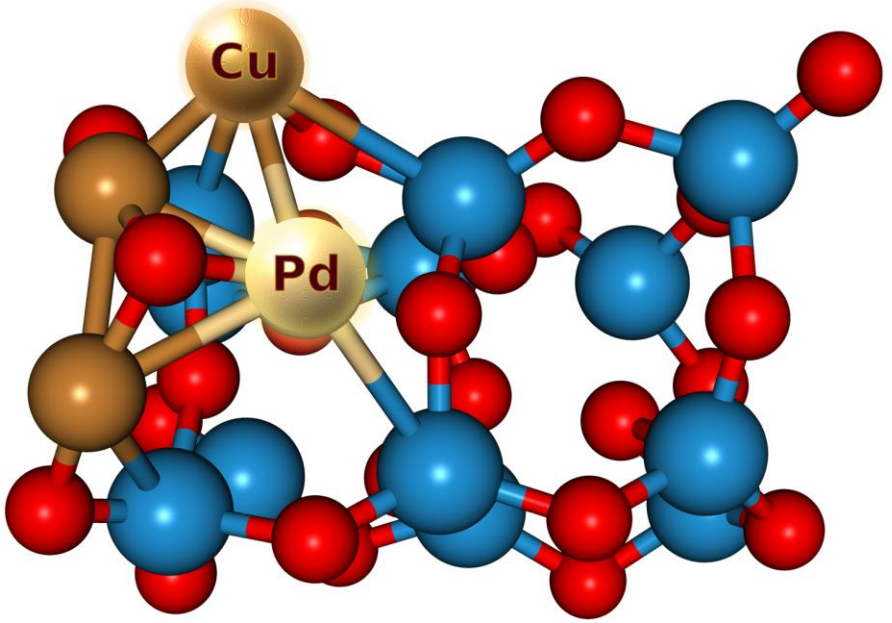
Exchange of the single Cu atom by single Pd atom

J. Heyrovský Institute of Physical Chemistry

Vajda group

GOAL

Mitigation of the greenhouse gas; catalytic performance optimization of Cu-tetramer clusters.



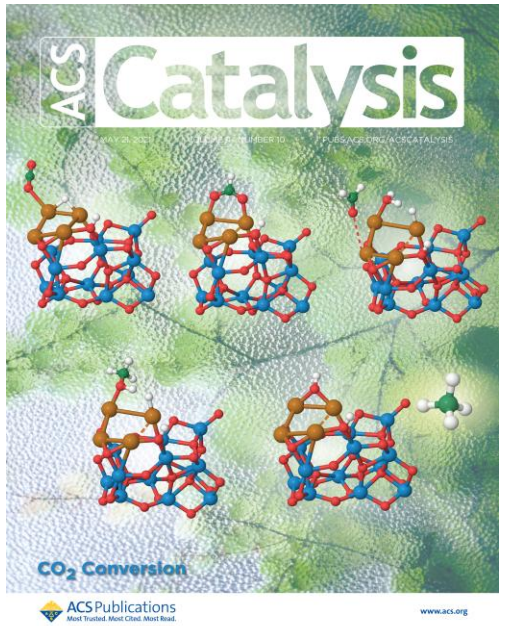
REACTION

CO_2 hydrogenation to methane and methanol.

- The morphology of substrate plays a crucial role in determining the activity of the catalyst as well as its cyclability.
- Nanostructured zirconia is more active than ALD.

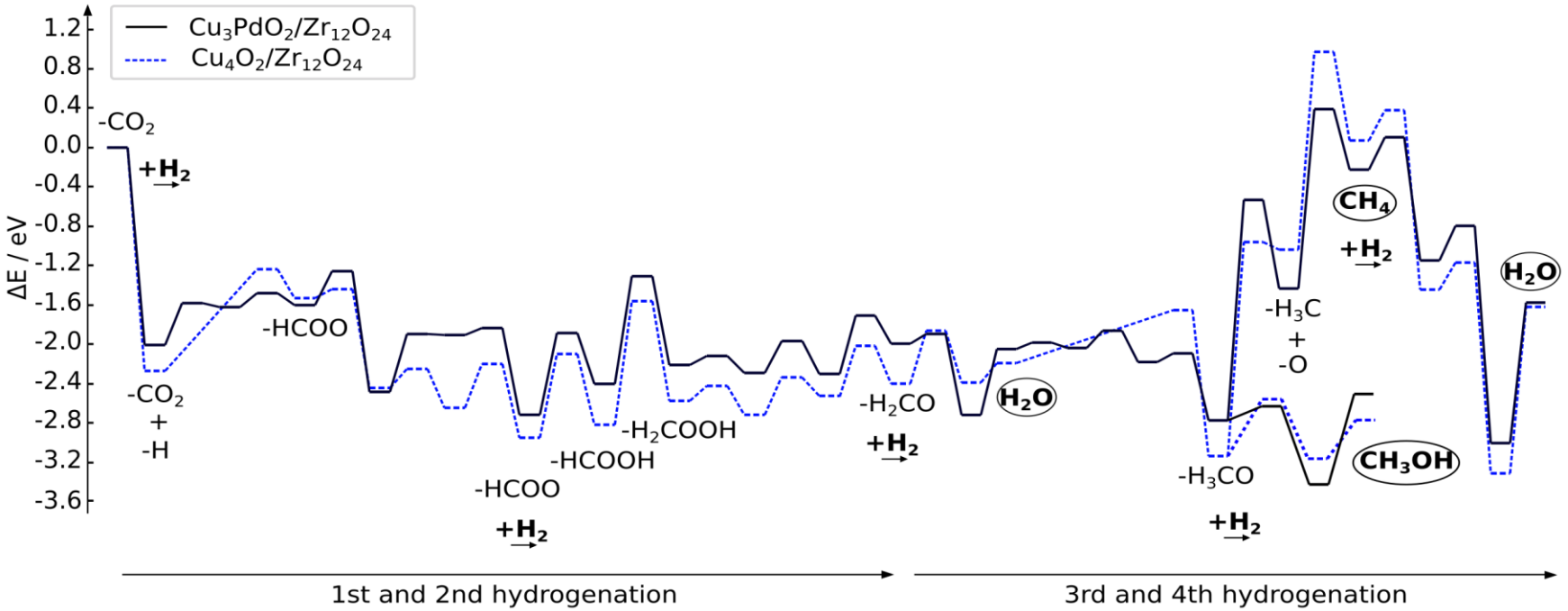
Table 1. Activation Energy for Cu Clusters on Zirconia Supports

	E_a	
catalyst	(kJ/mol)	(eV)
Cu_4/ALD ZrOx	70.92	0.74
Cu_{12}/ALD ZrOx	15.29	0.16
Cu_4/NS ZrOx	40.03	0.41
Cu_{12}/NS ZrOx	25.89	0.27

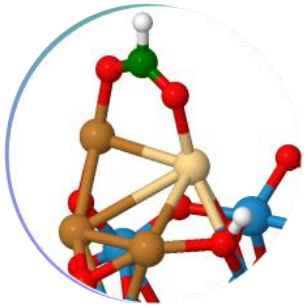


ACS Catalysis 2021; 11(10): 6210-24.

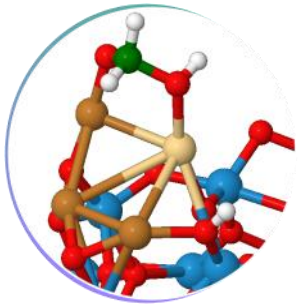
Comparison of energy profiles



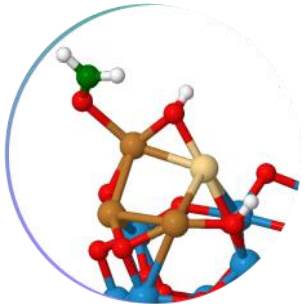
B3LYP/def2-TZVP
Dispersion correction GD3



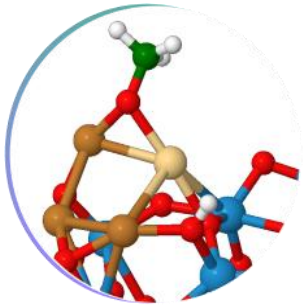
-HCOO



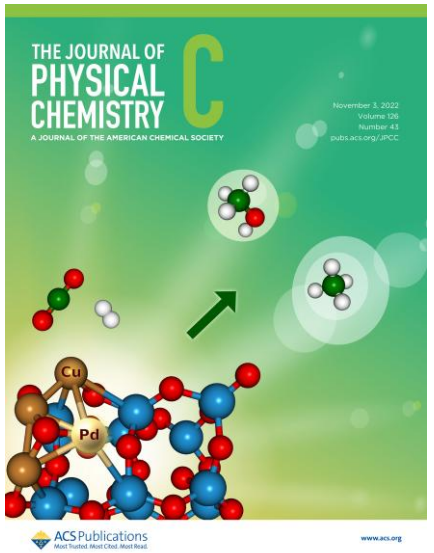
-H_2COOH



-H_2CO

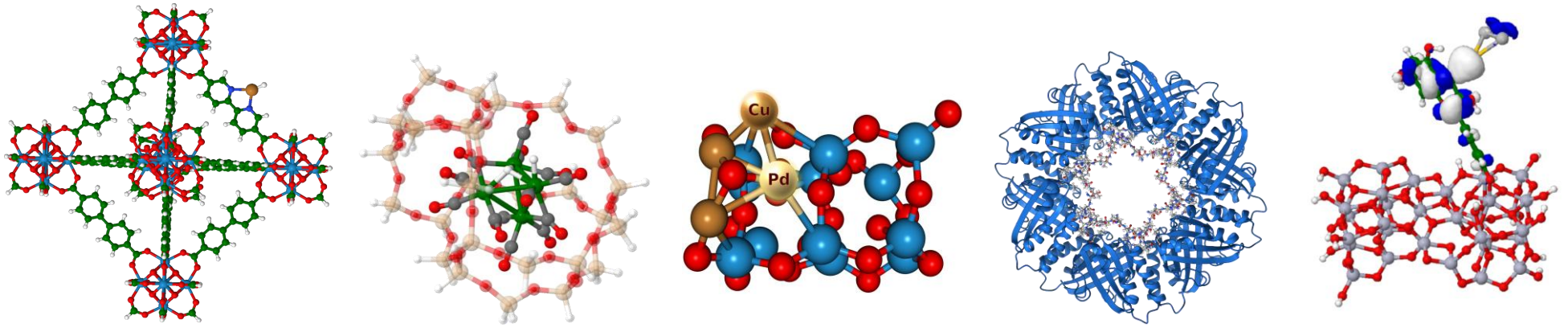


-H_3CO



J Phys. Chem. C. 2022; 126(43): 18306-12.

RESEARCH DIRECTIONS



I. Catalyst for H_2 production and storage

II. Catalyst for CO elimination

III. Catalyst for CO_2 conversion

IV. Artificial enzyme

V. DSSC system

COLLABORATORS

Experimental:

- Prof. R. O'Hair (University of Melbourne)
- Prof. S. Lang, Prof. B. Thorsten (University of Ulm)
- Dr. S. Vajda (Heyrovský Institute of Physical Chemistry)

CC team in Split

Theory:

- Prof. V. Bonačić-Koutecký (Centre of Excellence for Science and Technology, Split)
- Asst. Prof. M. Perić Bakulić (Faculty of Chemistry and Technology, Split)
- Assoc. Prof. Ž. Sanader Maršić (Faculty of Science, Split)
- Dr. M. Bužančić Milosavljević (Centre of Excellence for Science and Technology, Split)

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