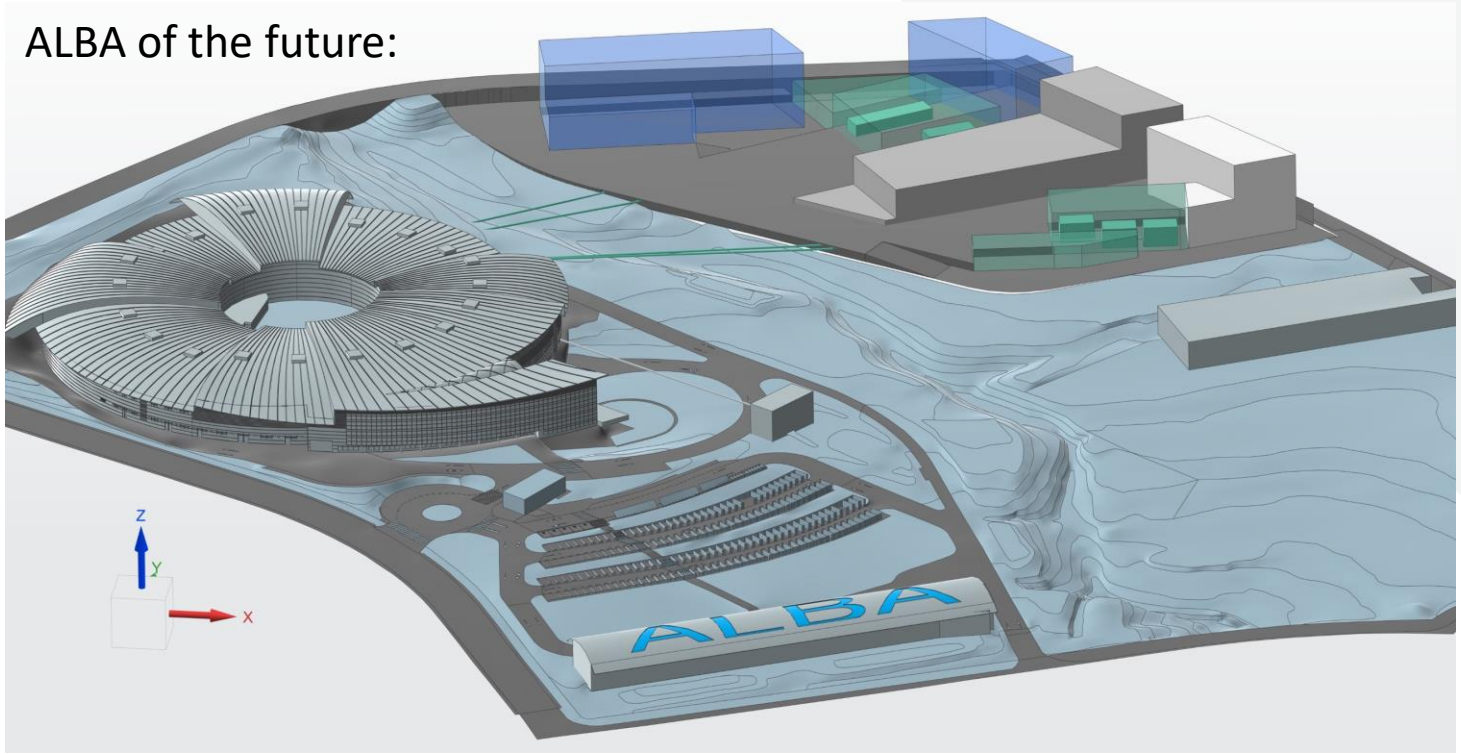
ALBA of the future:



Catalysis related study at the CLÆSS beamline

Alina Skorynina

06 November 2024 – Postdoc Day

- Key publications:

1. **A. Skorynina**, et al. *Journal of Materials Chemistry C*, 2024, IF 5.7
2. R.L. Vasile, *Journal of the American Chemical Society* 146.37 (2024): 25824-25831, IF **14.5**
3. G. O'Rourke, et al. *EES Catalysis*, 2.4 (2024): 1006-1018, IF n/a
4. O. Usoltsev, et al., *Small*, (2024): 2401184, IF **13.0**
5. E. Kozyr, et al. *Synchrotron Radiation*, 31.5 (2024), IF 2.6
6. R. S. Silva, et al. *CrystEngComm*, 26.24 (2024): 3240-3249, IF 2.6
7. T. Gosh, et al. *Chemical Science*, 15.29 (2024): 11488-11499 , IF **7.6**
8. I. Beckers, *ACS catalysis* 14 (2024): 7080-7086, IF **11.7**
9. O. Usoltsev, et al. *Small Methods*, 2024, 2301397, IF **12.4**
10. **A. Skorynina**, et al. *Inorganic Chemistry*, 2023, 62(17), 6608–6616, IF 4.6
11. E. Kozyr, et al. *Catalysts* 2023, 13 (2), 414, IF 3.9
12. G. O'Rourke, et al. *Chemical Science* 2023, 15, IF **8.4**
13. O.A. Usoltsev, et al. *Applied Surface Science*, 2023, 614, 156171, IF 6.7

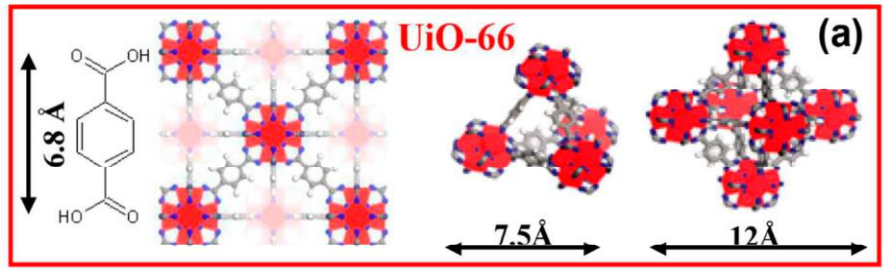
- During my PhD: project management in 4 grants, 12 publications, 30+ conferences, *h*-index = 5
- During ALBA stay: 1 ReMade project, organizing HERCULES2024 and 2025, developing the Harrick Solid-gas reactor, 13+ publications, 2 conferences, *h*-index = 8

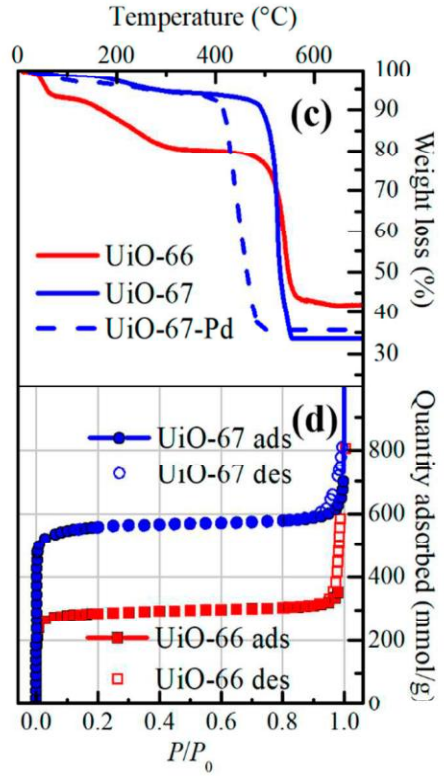
Key Work from the Past:

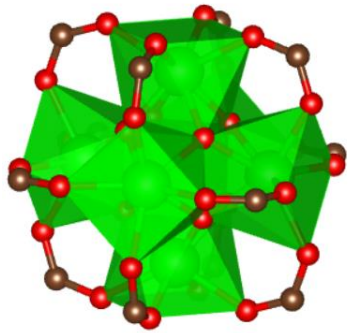
Prof. Unni Olsbye

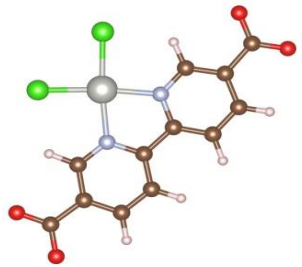
Prof. Silvia Bordiga

- Reduction of greenhouse gas emissions and utilization of CO_2 as a feedstock
- MOFs promote a more uniform distribution of metal nanoparticles, increasing the accessibility of active sites
- Flexibility in MOF-catalyst design to incorporate a variety of metals and functional groups





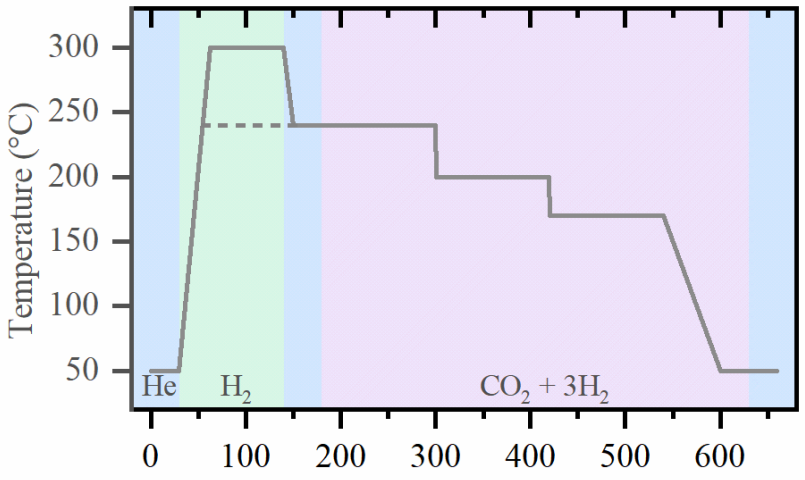


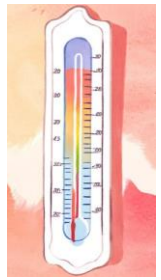


A. Bugaev, A. Skorynina, et al *Cat. Tod*. 336 (2019) 33–39.

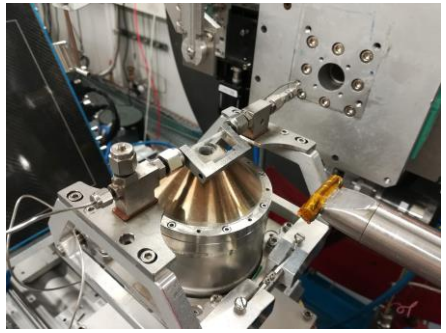
A. Skorynina, et al. *Journal of Materials Chemistry C*, 2024.

Operando experiment on CO_2 hydrogenation





Act.: 1.4 mL/min H_2 and 8.6 mL/min He, 300 or 240 °C, 30 min
Reac.: 7.5, 2.5, and 10 mL/min of H_2, CO_2, and He, respectively
240, 200, 170 and 50 °C, 1 or 8 bar, 2 h

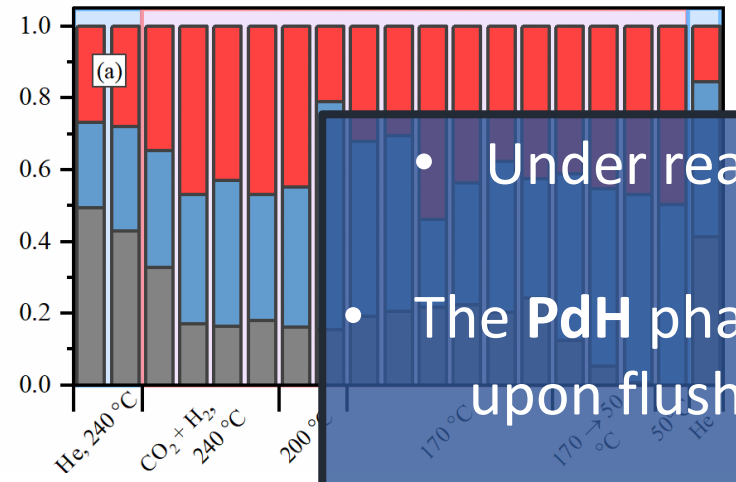


Skorynina, et al. *Journal of Materials Chemistry C* 12.10 (2024): 3564-3572.

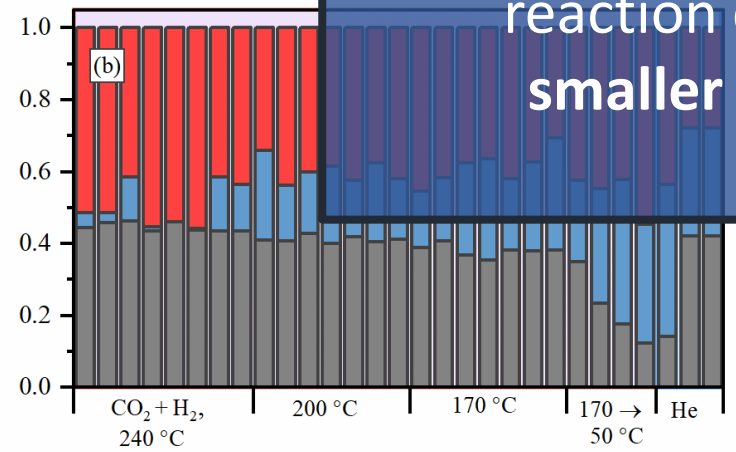
A. Bugaev, A. Skorynina, et al *Cat. Tod*. 336 (2019) 33–39.
A. Skorynina, et al. *Journal of Materials Chemistry C*, 2024.

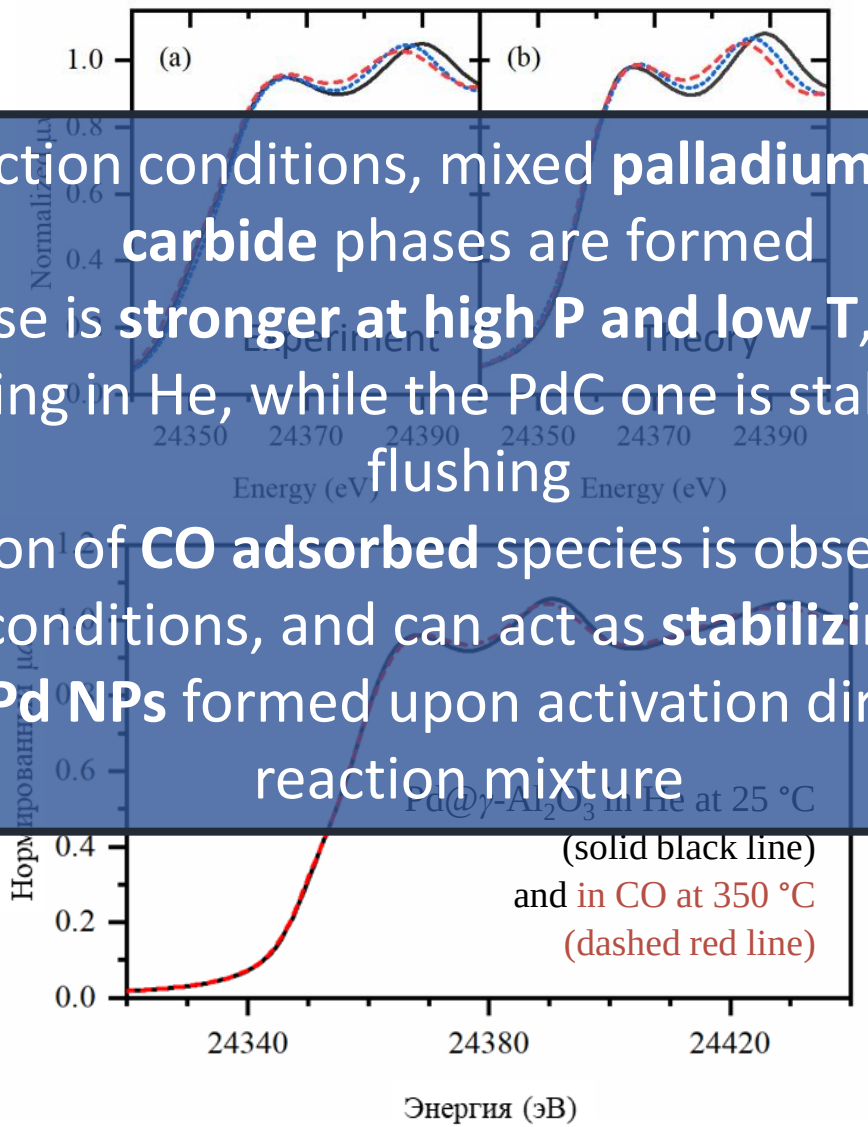
Operando experiment on CO_2 hydrogenation

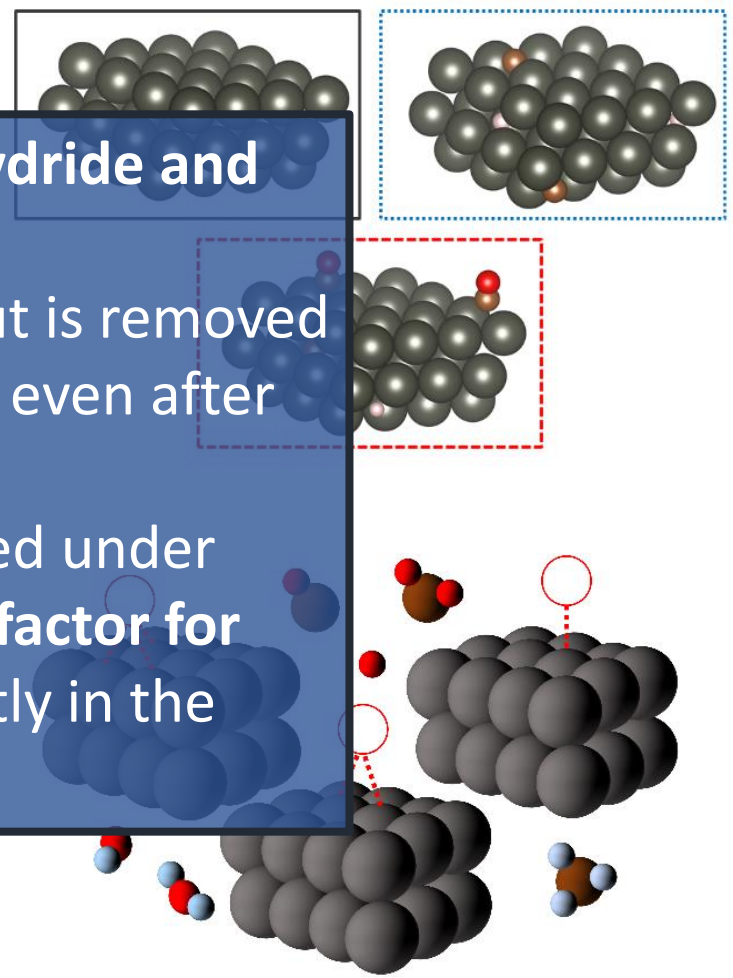
300 °C in H_2, 8 bar



240 °C in $H_2 + CO_2$, 1 bar



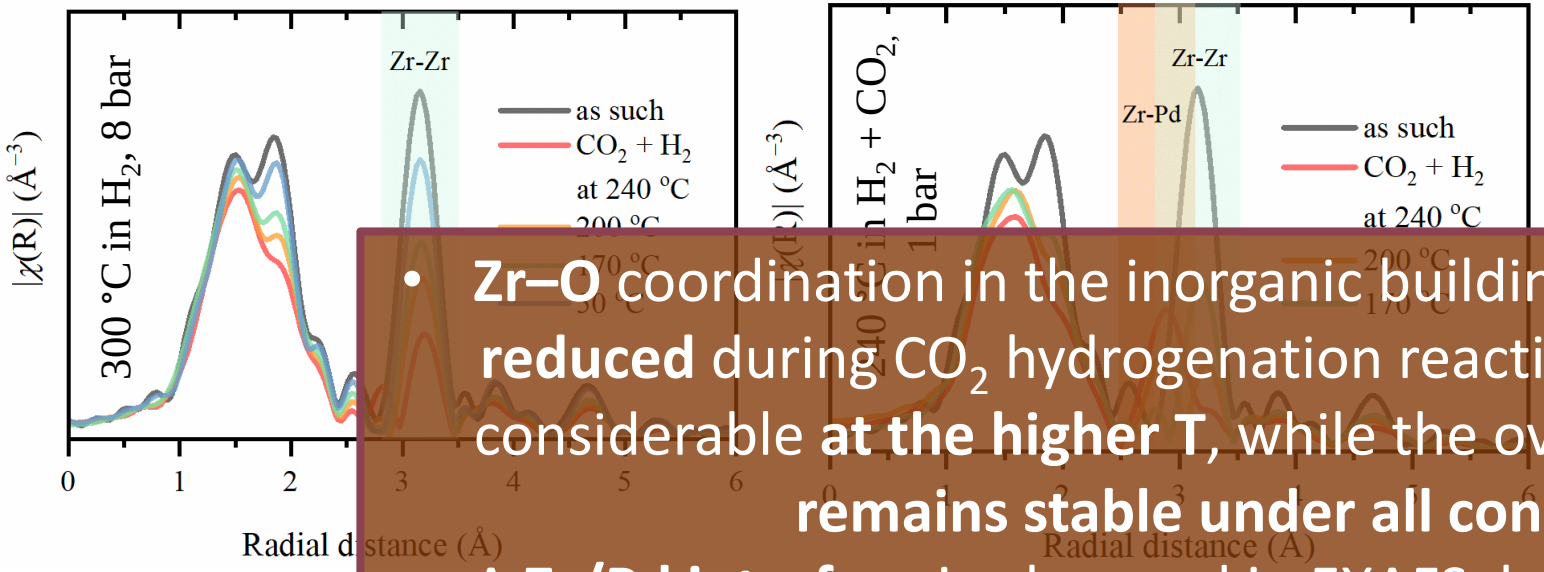




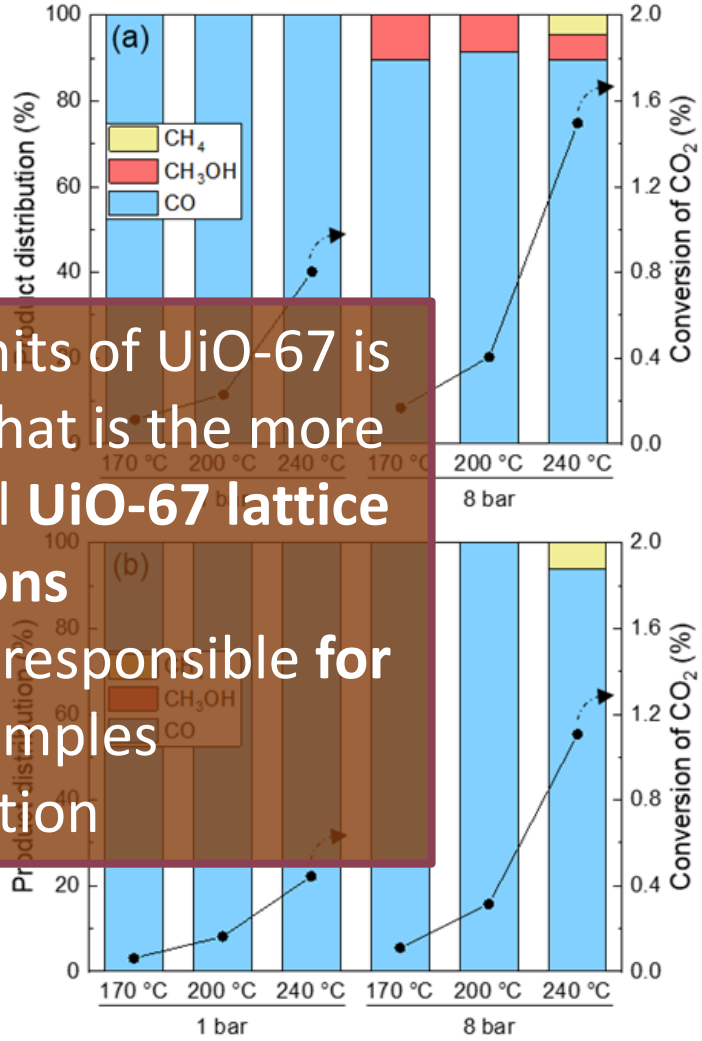
- Under reaction conditions, mixed **palladium hydride and carbide** phases are formed
- The **PdH** phase is **stronger at high P and low T**, but is removed upon flushing in He, while the PdC one is stable even after flushing
- Formation of **CO adsorbed** species is observed under reaction conditions, and can act as **stabilizing factor for smaller Pd NPs** formed upon activation directly in the reaction mixture

A. Skorynina, et al. *Journal of Materials Chemistry C*, 2024.

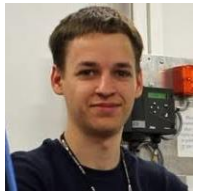
Operando experiment on CO_2 hydrogenation



- **Zr–O** coordination in the inorganic building units of UiO-67 is **reduced** during CO_2 hydrogenation reaction that is the more considerable **at the higher T**, while the overall **UiO-67 lattice remains stable under all conditions**
- A **Zr/Pd interface** is observed in EXAFS, being responsible **for methanol formation** in UiO-67-Pd samples
- CO is the main product of the reaction








Skorynina, et al. *Journal of Materials Chemistry C* 12.10 (2024): 3564-3572.

Goal for the ALBA Stay:

Previous talk summary: after 3 months from joining ALBA: showed achieved technical skills for users support & early involvement in ReMade projects

Motivation: interest in the job and need of building the necessary technical and scientific skills, user support to be incorporated in Spanish institutions, ideally at ALBA

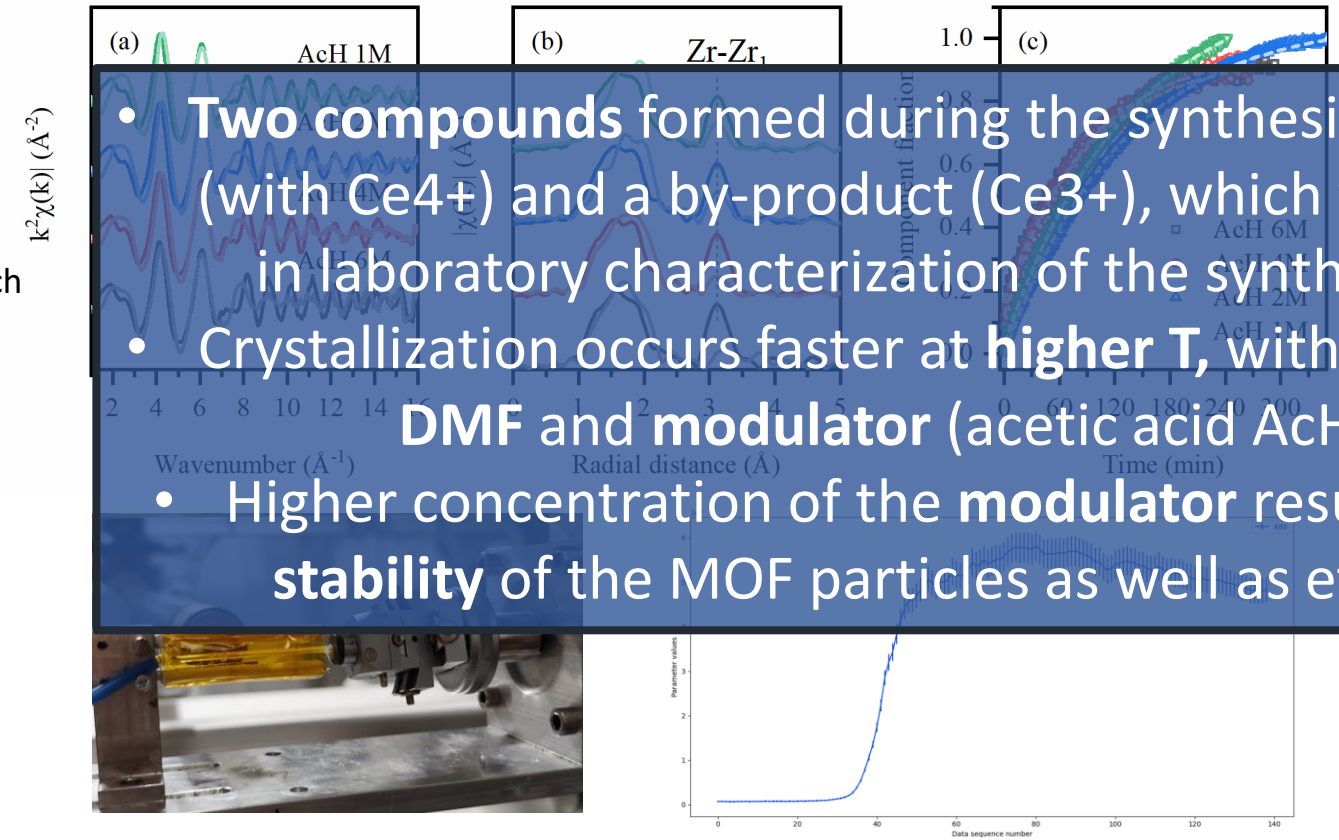
Key collaborators and networks:

- Patricia Conceptión (ITQ, Valencia)
- Felipe Gándara (CSIC, Madrid)
- Diego Cazorla Amoros (Universidad de Alicante, Alicante)
- Vitaly Sushkevich and Aram Bugaev (PSI, Switzerland)
- Unni Olsbye (UIO, Norway)
- Dirk de Vos (KU Leuven, Belgium)

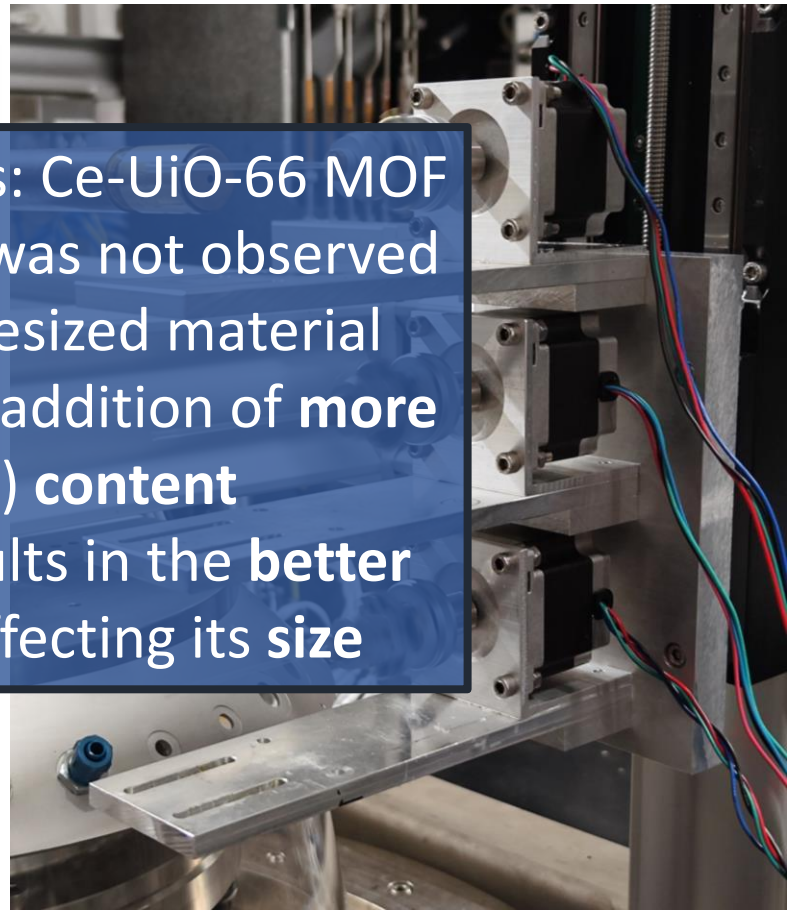
Results and activities from already performed work: In situ size-shape-controlled synthesis

Dr. Vitaly Sushkevich

Monometallic Zr- or Ce-UiO-66 and bimetallic Ce/Zr-UiO-66



- **Two compounds** formed during the synthesis: Ce-UiO-66 MOF (with Ce4+) and a by-product (Ce3+), which was not observed in laboratory characterization of the synthesized material
- Crystallization occurs faster at **higher T,** with addition of **more DMF** and **modulator** (acetic acid AcH) **content**
- Higher concentration of the **modulator** results in the **better stability** of the MOF particles as well as effecting its **size**



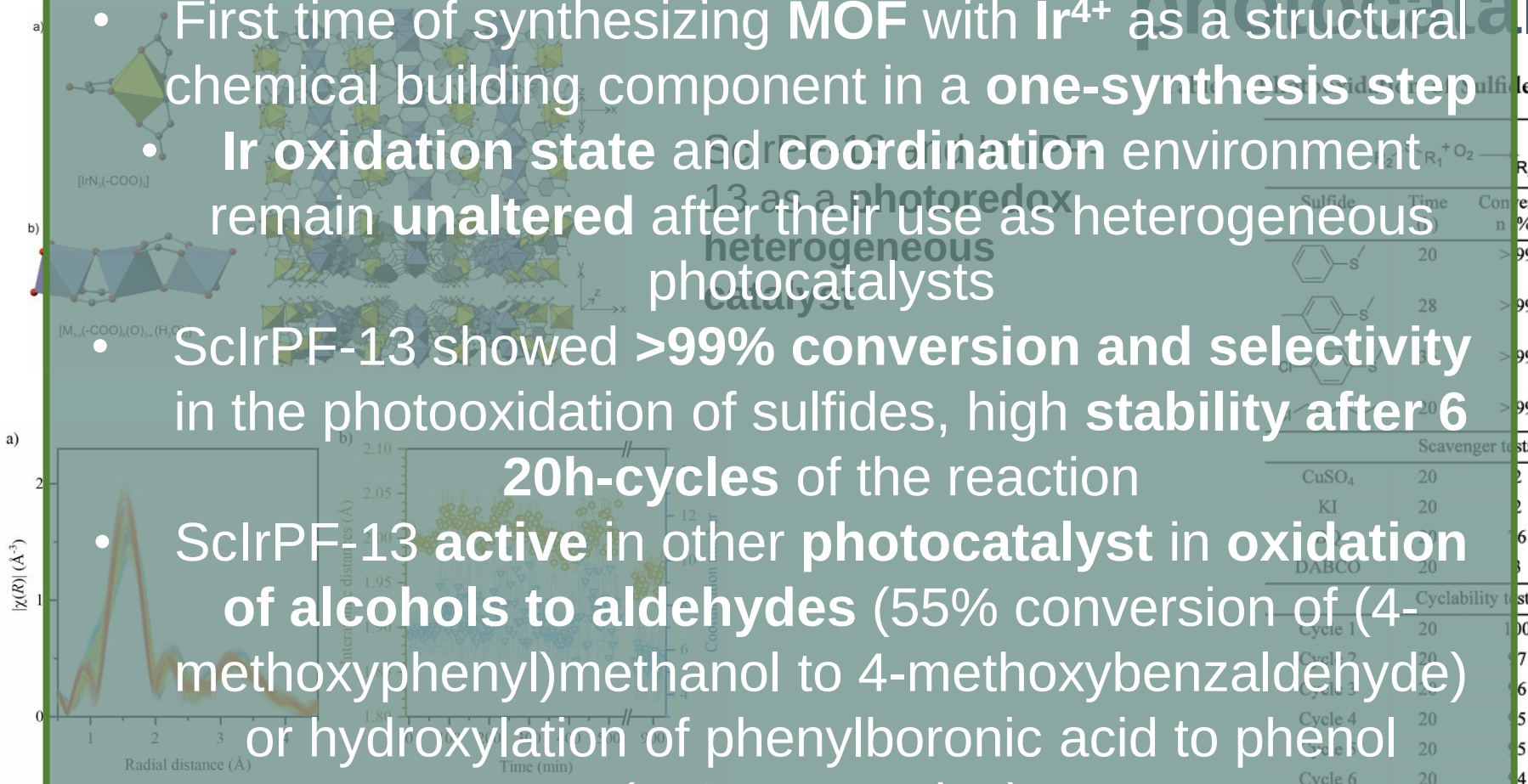
A. Skorynina, *In process*, 2025

Results and activities from already performed work:

Multi-metal MOFs as heterogeneous photocatalysts

Dr. Felipe Gándara

- First time of synthesizing **MOF** with **Ir^{4+}** as a structural chemical building component in a **one-synthesis step**
- **Ir oxidation state** and **coordination** environment remain **unaltered** after their use as heterogeneous photocatalysts
- ScIrPF-13 showed **>99% conversion and selectivity** in the photooxidation of sulfides, high **stability after 6 20h-cycles** of the reaction
- ScIrPF-13 **active** in other **photocatalyst** in **oxidation of alcohols to aldehydes** (55% conversion of (4-methoxyphenyl)methanol to 4-methoxybenzaldehyde) or hydroxylation of phenylboronic acid to phenol (55%conversion)



les with ScIrPF-13[a]

Sulfide	Time	Conversion (%)	Selectivity to sulfoxide (%)
	20	>99	100
	28	>99	100
		>99	100
		>99	100
Scavenger tests[b]			
$CuSO_4$	20	2	
KI	20	2	
		6	
DABCO	20	8	
Cyclability tests[b]			
Cycle 1	20	100	99
Cycle 2	20	97	99
Cycle 3	20	96	99
Cycle 4	20	95	99
Cycle 5	20	95	99
Cycle 6	20	94	99

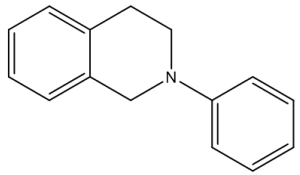
[a]Photooxidation conditions: sulfide (0.135 mmol), catalyst (2 mol% Ir), acetonitrile (0.5 mL), irradiated with blue LED light (420 nm, 2 × 30W) at RT under O_2 balloon atmosphere. [b]Carried out with methylphenylsulfide.

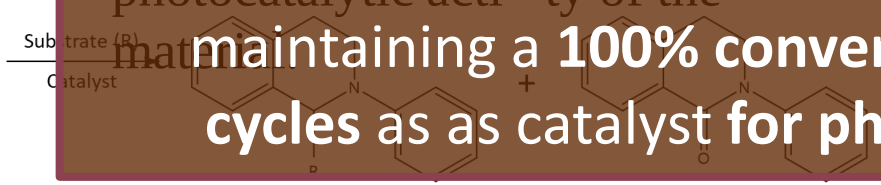
R.L. Vasile, *Journal of the American Chemical Society* 146.37 (2024): 25824-25831.

Results and activities from already performed work: Multi-metal MOFs as heterogeneous photocatalysts

Dr. Felipe Gándara

- **Different multimetal MOFs** based on tritopic H_3BTB and tetratopic H_6TCPP linkers were synthesized, using **identical multimetal *m*BUs** as precursors
- The **incorporation** of specific **Co** sites in the SBU results in an **enhancement** of the **photocatalytic activity** in comparison with its single-metal analogue MOF
- **Ga7Co-TCPP** demonstrated an excellent performance maintaining a **100% conversion** value even after **5 recycling cycles** as as catalyst **for photocatalytic aza-Henry reaction**





Entry	MOF	Drying	Conv. (%)	Sel. A (%)
1	Ga-TCPP	Air	95	87
2	GaNi-TCPP	Air	92	86
3	Ga7M-TCPP	Air	97	90
4	Ga-TCPP	Freeze	97	80
5	GaNi-TCPP	Freeze	83	100
6	Ga7M-TCPP	Freeze	100	100

[a]Reaction conditions: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (15 µL, 0.08 mmol), nitrometane (0.6 mL), catalyst (5-6 mg, 1.0 %), blue LED ring light, at room temperature during 24 h in air. Selectivity of the products A and B were determined by 1H-NMR.

C. López-García, A. Skorynina, *Small Structures* (IF 13.9), 2024 *Under review*

Approach

Hydrogenation of alkenes to alkanes

Dr. Patricia Concepción

INSTITUTO DE TECNOLOGÍA QUÍMICA

- Pd, Rh, Pt and Ni catalysts
- Plastic and polymer industry

Harrick cell commissioning under real catalytic conditions

- Compatible with vacuum cube
- Accessing energies below 6 keV:
  - *a.* L_3-edges of the following transition metals (**Ru** 2838 eV, **Rh** 3004 eV, Pd 3173 eV, Ag 3351 eV, In 3730 eV, Sn 3929 eV, etc.)
  - *b.* *K*-edges of S, Cl, K, Ca, Sc, Ti, V (which are not reachable with ITQ solid gas reactor)
- Small inner volume
- Wider range of temperatures and pressures
- Suitable for in situ gas/liquid circulations
- Short space between window and the sample (2-3 mm)
- Easy replacement of windows

- Long term goals:
  - Deepen expertise in catalysis
  - Develop technical approach to address complex catalytic reactions
  - Engineer tunable synthesis approaches to enhance catalyst performance
- Measure for success:
  - Publication
  - Conferences
  - Grants

Summary:

Group of Dr. Patricia Concepción
"Heterogeneous Catalysis to Reveal New Capabilities of the Harrick Solid-Gas Reactor"

Dr. Felipe Gándara
"Tailored Multimetal MOFs for Enhanced Photocatalytic Applications"

Group of Prof. Dirk De Vos
"Ru-, Rh-, Pd-complexes for PVC Recycling"
(Homogeneous catalysis)

Group of Prof. Unni Olsbye
"MOFs for CO_2 hydrogenation"

Group of Prof. Diego Cazorla
"Design of Biomass-Derived Activated Carbon Catalysts for Hydrogen Production"

Dr. Vitaly Sushkevich
"Mechanisms of the formation of MOFs"

Dr. Aram Bugaev
"Study of noble metal catalysts phases under real catalytic processes"