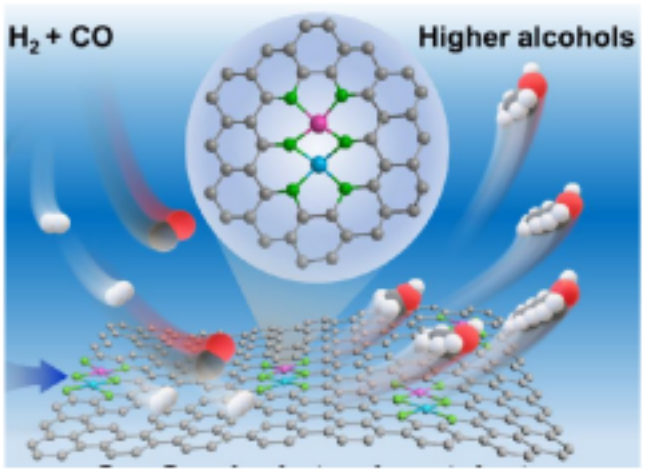
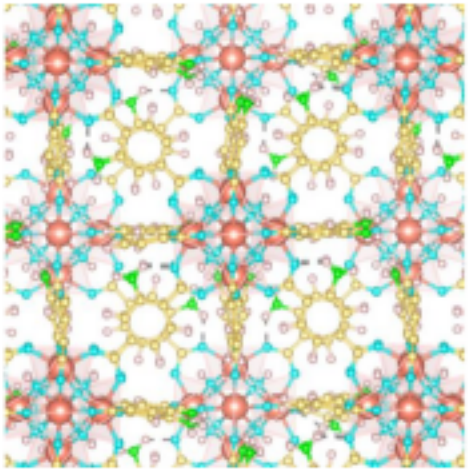
Targeted electronic structure modification in catalysis: a case study of dual-metal catalyst for CO hydrogenation

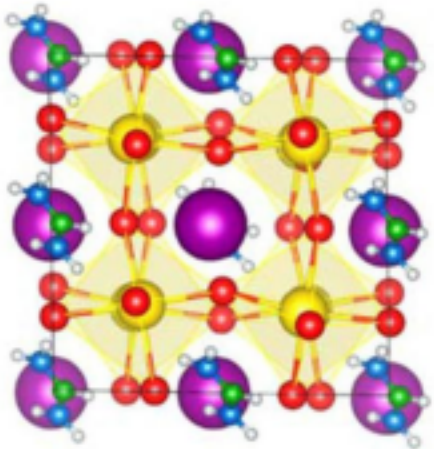
Olga A. Syzgantseva

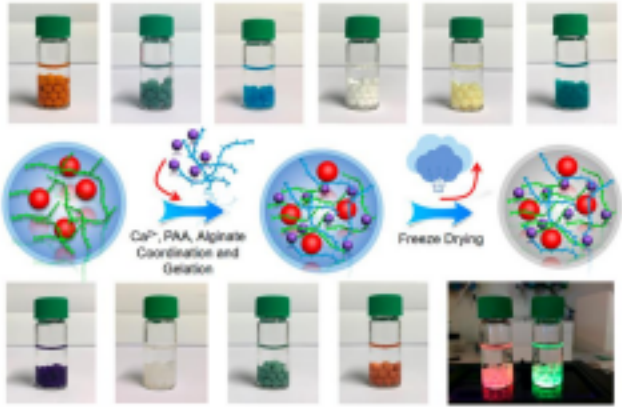
Hybrid organic-inorganic catalysts





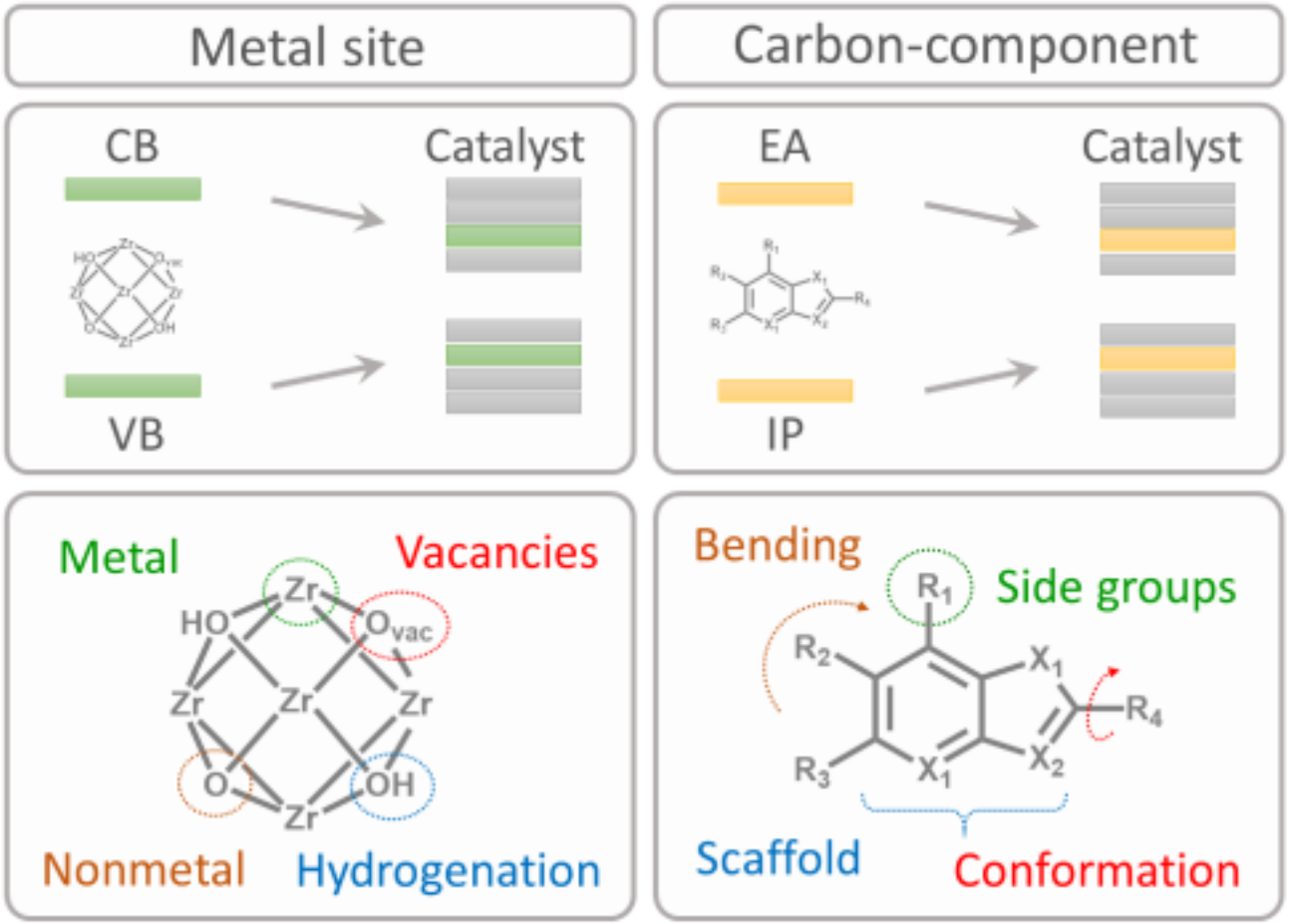
- MOF
- Perovskites
- Polymer composites
- Metals in CN-materials





CCS Chemistry, **2022**, 202201930
APL Materials **2019**, *7, 041110*
JACS **2020**, *142*, 13415–13425
JPCL **2019**, 10, 5041–5046

Compositional leverages

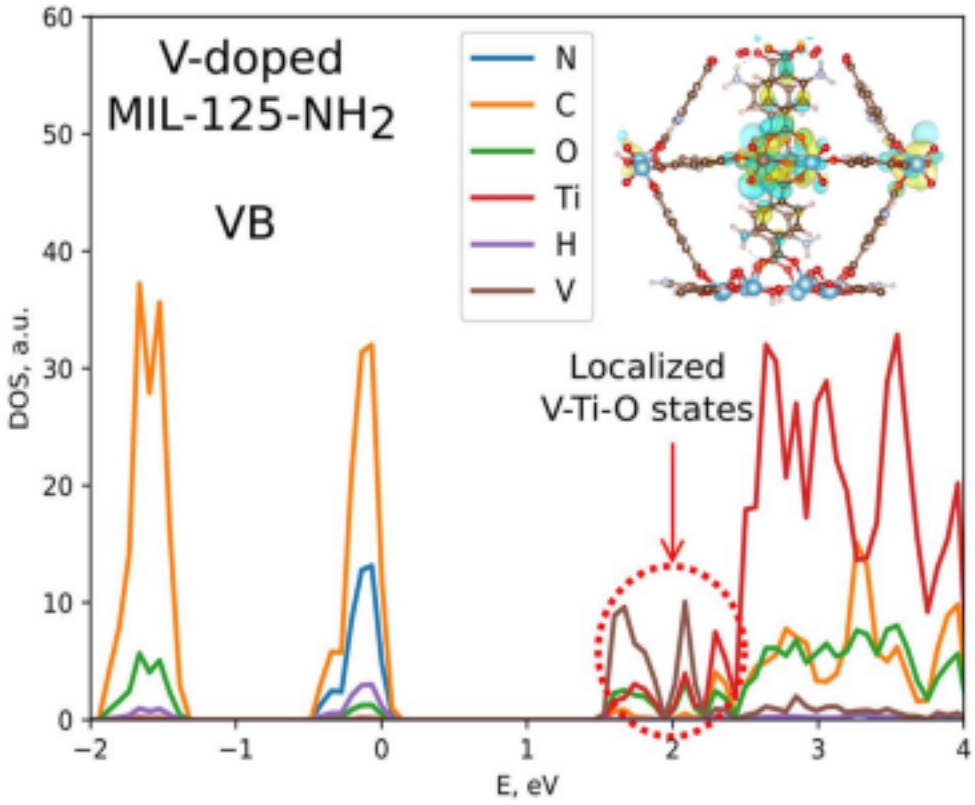


M.A. Syzgantseva *et al.* *J. Am. Chem. Soc.* **2019**, 141, 15, 6271–6278

M.A. Syzgantseva *et al.* *ACS Appl. Mater. Interfaces* **2020**, *12*, 15, 17611–17619

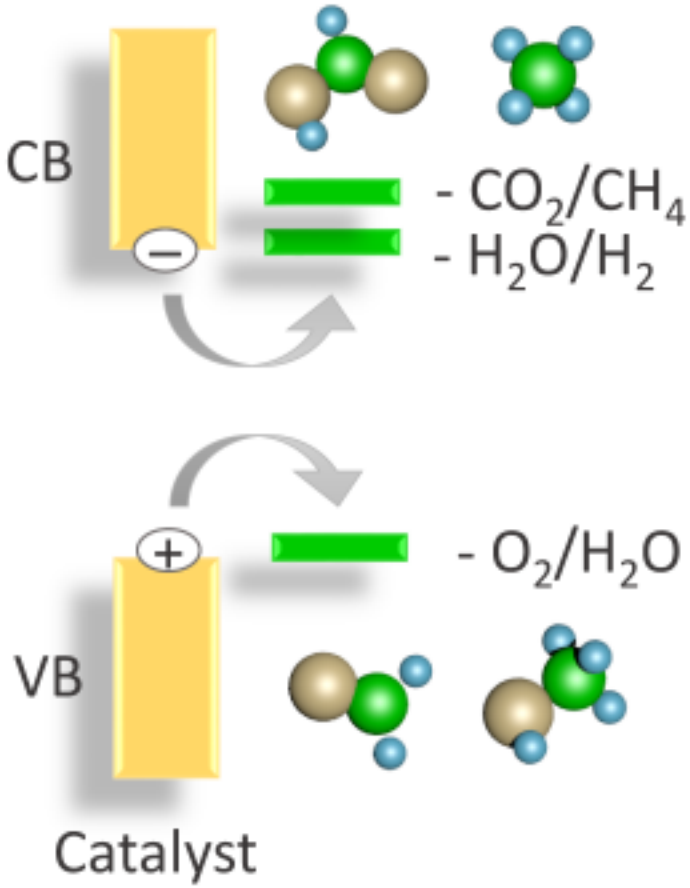
Targeted electronic structure modification

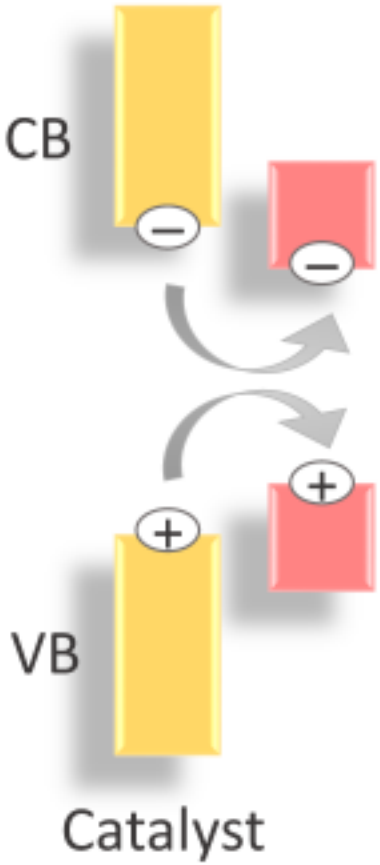
- Band alignment
- Work function
- Localization
- Charge separation
- Density-of-states



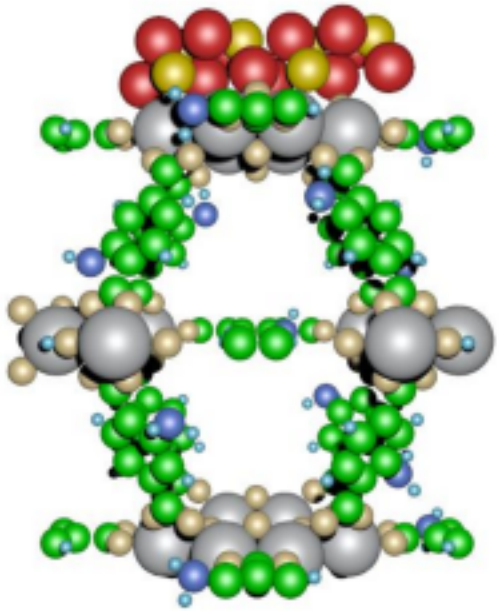
M.A. Syzgantseva *et al. J. Am. Chem. Soc.* 2019, 141, 15, 6271–6278

Appropriate band alignment for efficient reduction





Co-catalyst



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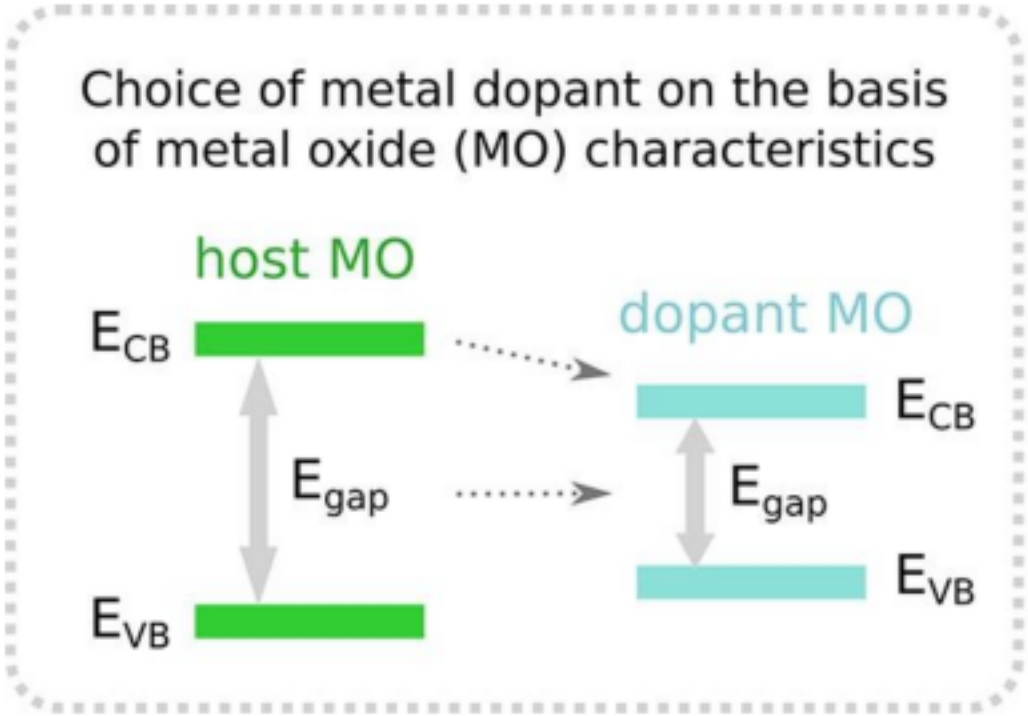
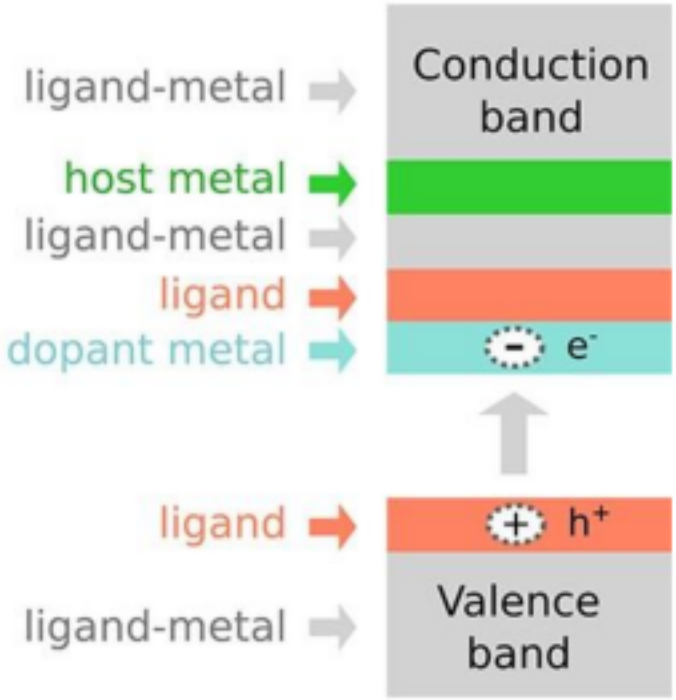
2020, *12*, 15, 17611–17619

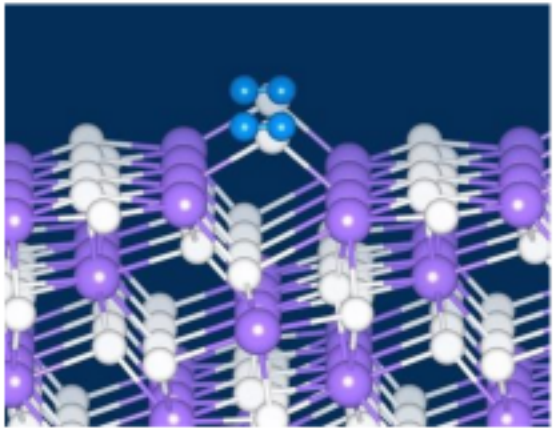
Changing the reducibility in mixed-metal systems



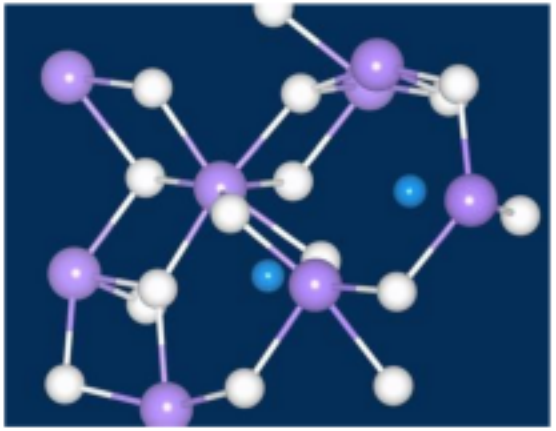


M.A. Syzgantseva *et al. J. Am. Chem. Soc.* **2019**, 141, 15, 6271–6278
M.A. Syzgantseva *et al. ACS Appl. Mater. Interfaces* **2020**, *12*, 15, 17611–17619

Reduction reactions



Spontaneous hydrogen dissociation on ZrO_{2-x}



Oxygen migration on ZrO_{2-x}

Syzgantseva O.A. *et al.* *J. Phys. Chem. C*, **2012**, *116*, 6636–6644

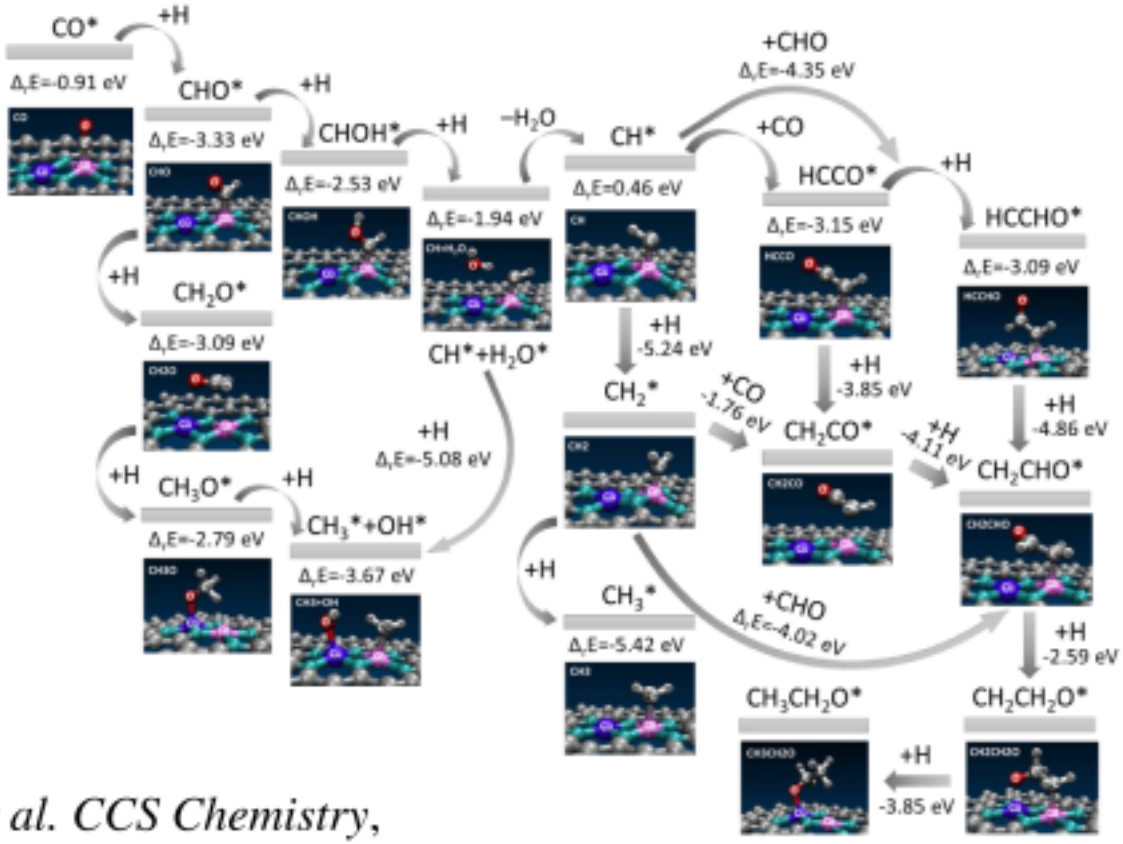
H O Zr

Reduction of CO, CO_2 to form CH_4, CH_3OH, CH_2O, $HCOOH$

Higher alcohol synthesis (HAS) from syngas

Reaction mechanism

DFT investigation of the reaction mechanism and adsorption intermediates



G. Chen, O.A. Syzgantseva, *et al. CCS Chemistry*, **2022**, doi: 10.31635/ccschem.022.202201930

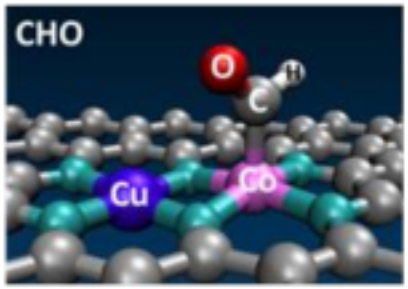
Key reaction steps

- C – O bond splitting
- C – C coupling
- Hydrogenation of C_{2+} intermediate

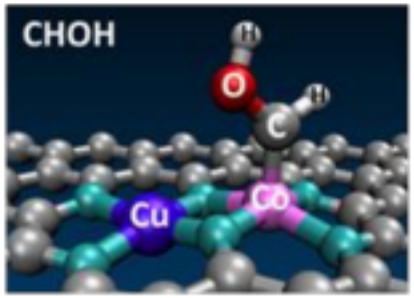
Reaction mechanism

CHO* +H CHOH* +H

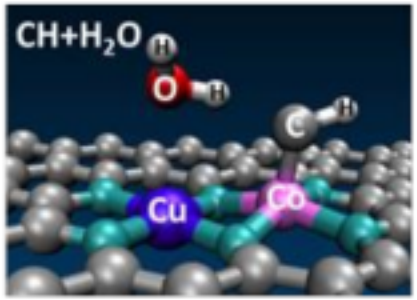
$\Delta_r E$=-3.33 eV



$\Delta_r E$=-2.53 eV



$\Delta_r E$=-1.94 eV



$CH^* + H_2O^*$

C – O bond splitting favored by high CH_x adsorption energy on Co-sites

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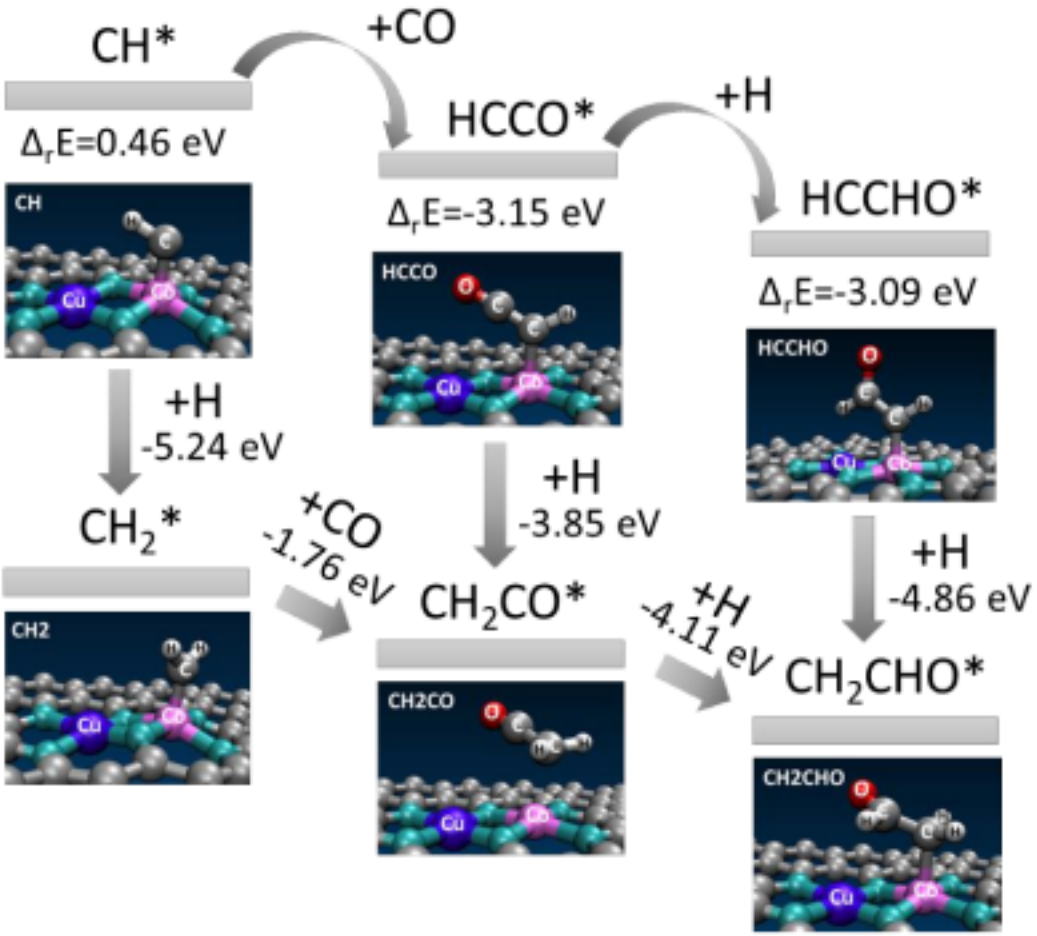
Reaction mechanism



C – C coupling is barrierless due to high reactivity of CH_x on Co sites

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Reaction mechanism

Hydrogenation of C_{2+} intermediate is efficient due to the N hydrogen tank, enabling hydrogen transfer towards species adsorbed on Co-sites. Selectivity towards alcohol is ensured by Cu adsorption states, responsible for stabilizing O containing species.

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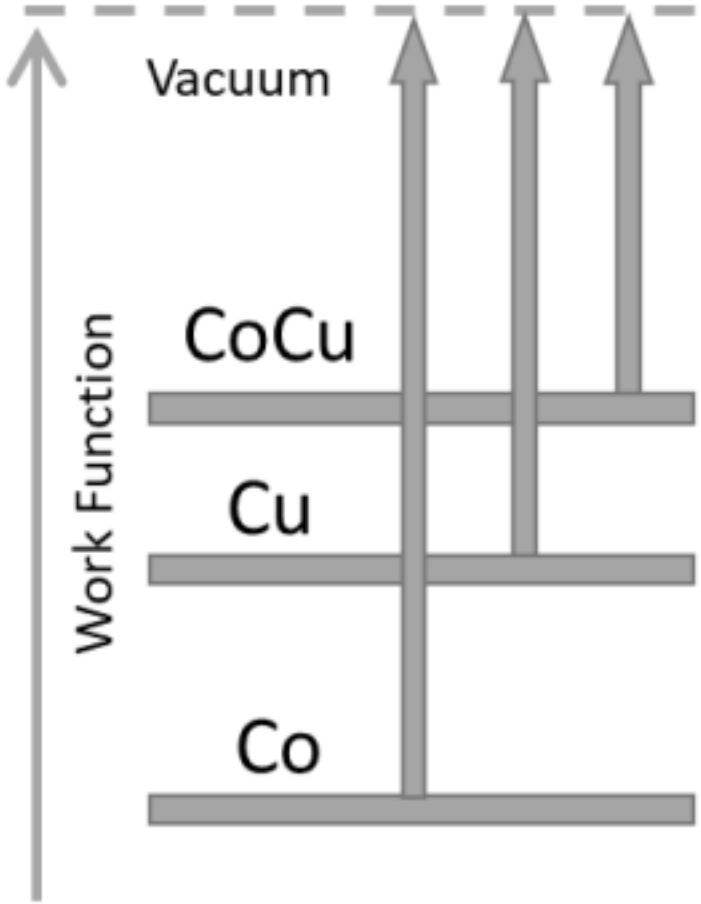
doi: 10.31635/ccschem.022.202201930

Origins of the efficiency



Facilitated charge transfer between the catalyst and the adsorbate due to lower work-function

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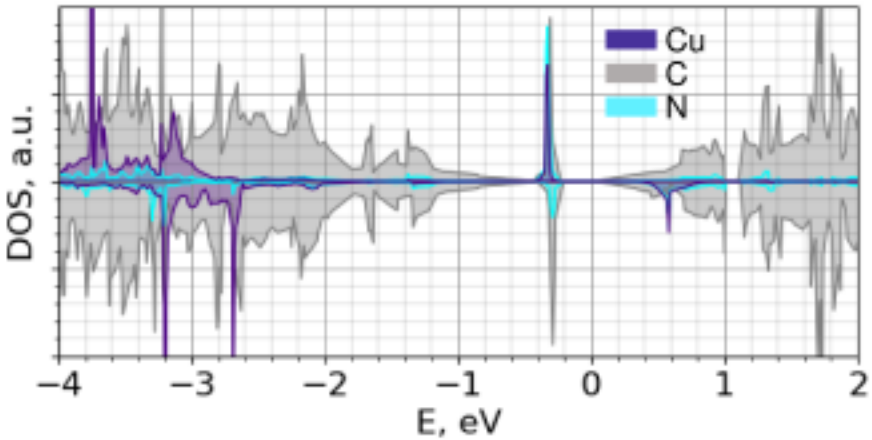
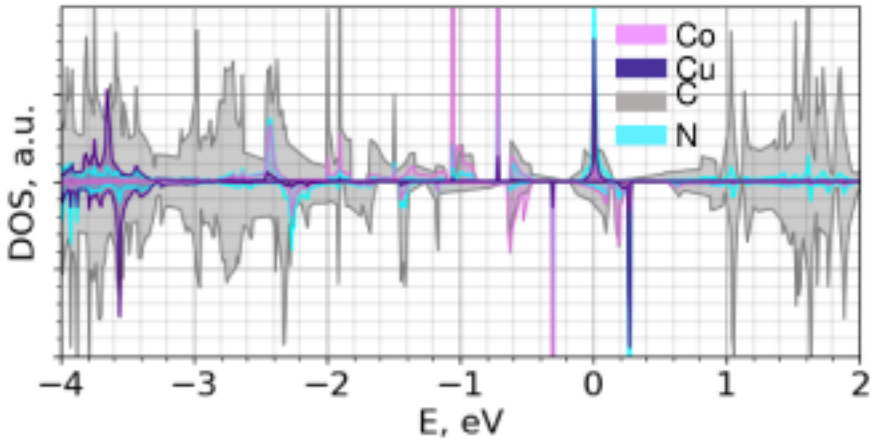
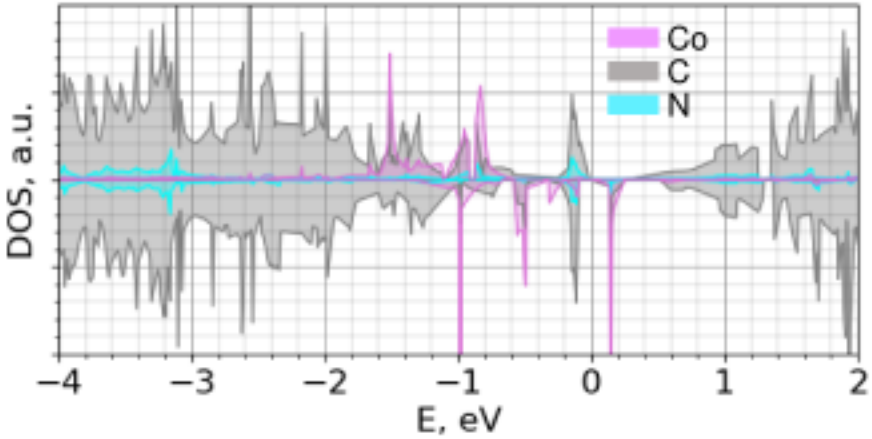
Origins of the efficiency







Increased DOS near E_{Fermi}

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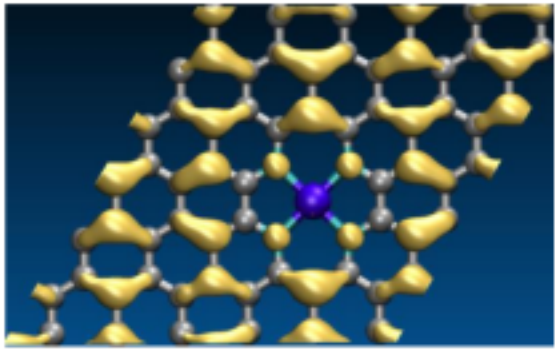
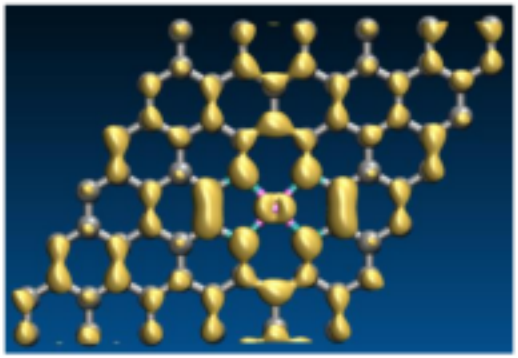
Origins of the efficiency

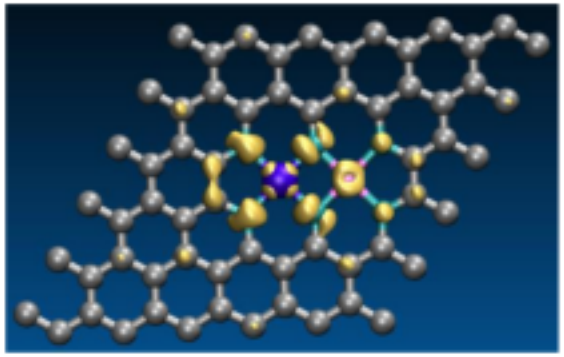
Cu-CN



Co-CN



CoCu-CN



Enhanced metal-centered (Co/Cu) localization

Facilitated charge transfer between catalyst and adsorbants

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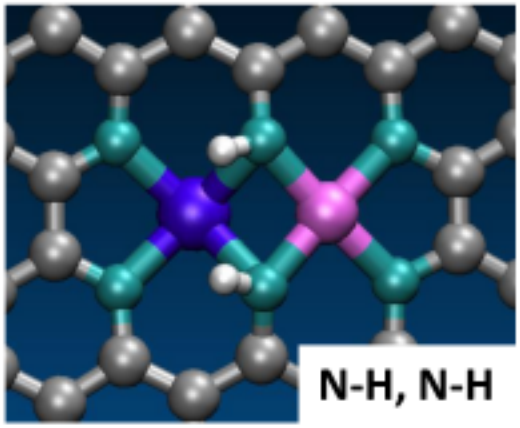
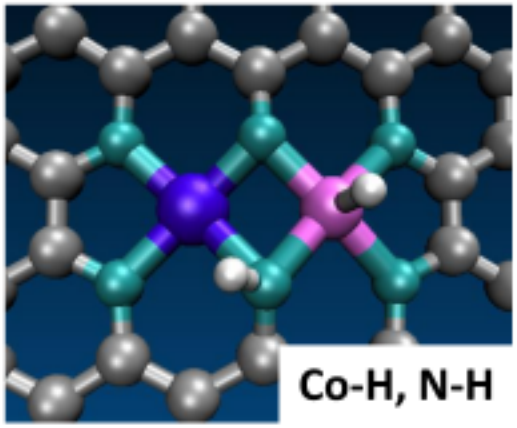
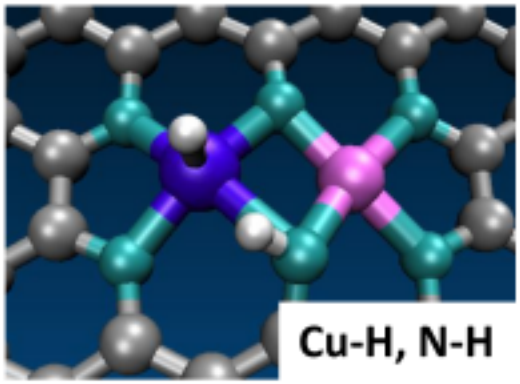
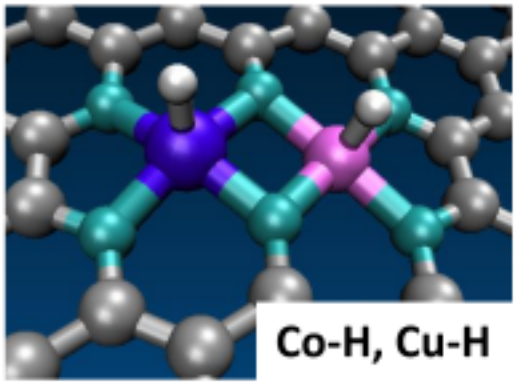
Origins of the efficiency









Adsorption mode	$E_{ads}(H_2)$, eV
N – H, N – H	-0.68
Co – H, N – H	-0.22
Cu – H, N – H	1.06
Co – H, Cu – H	1.77

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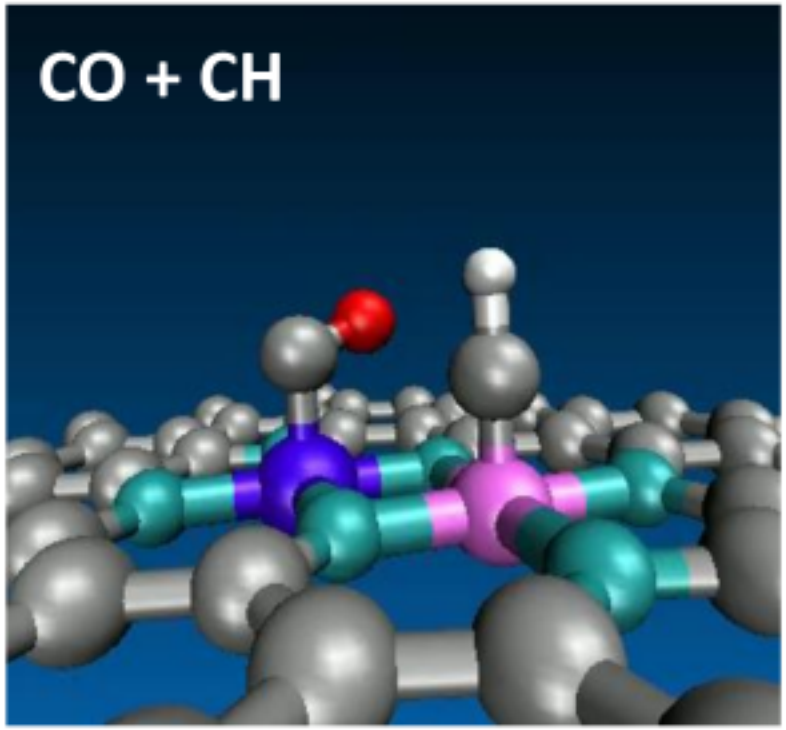
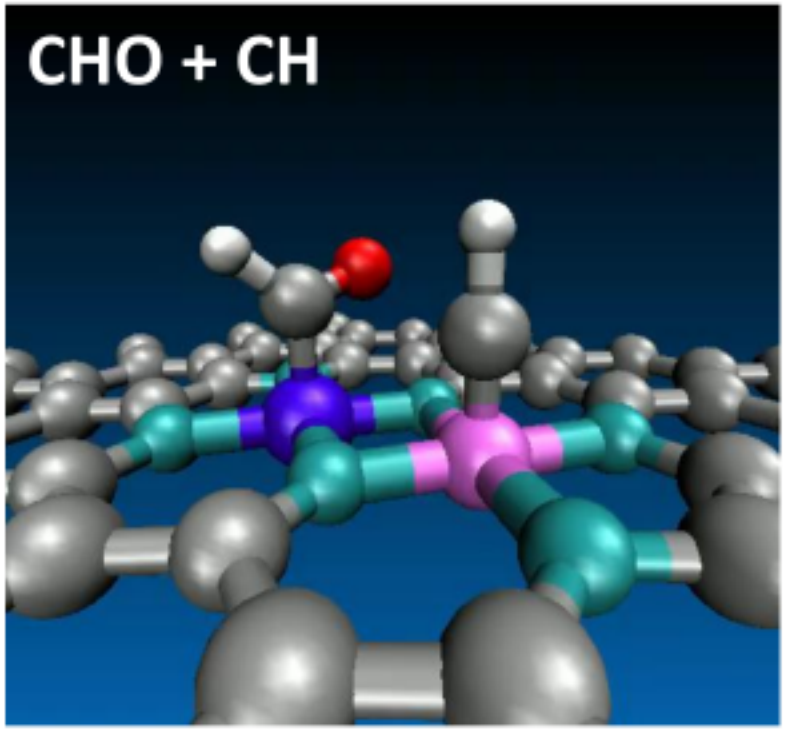
Barrierless C – C coupling





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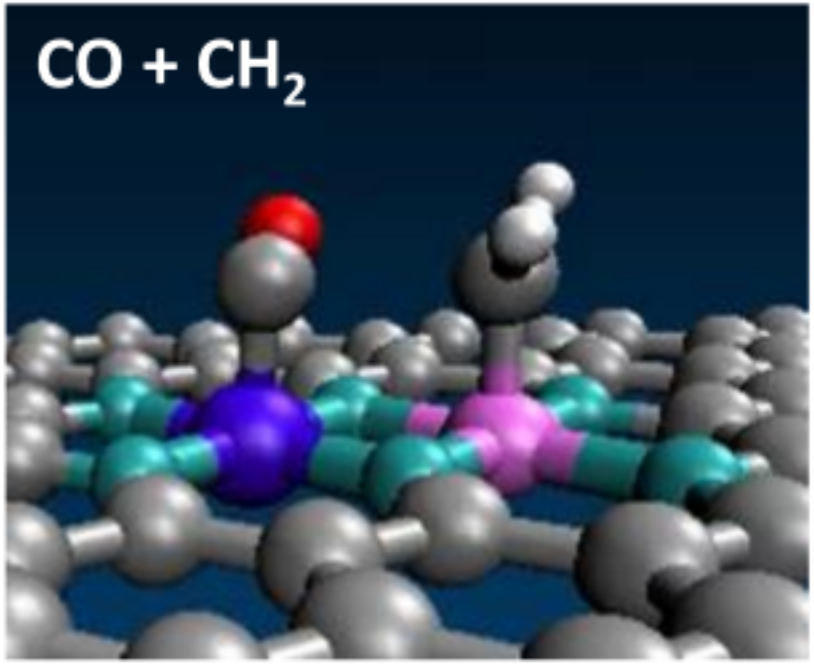

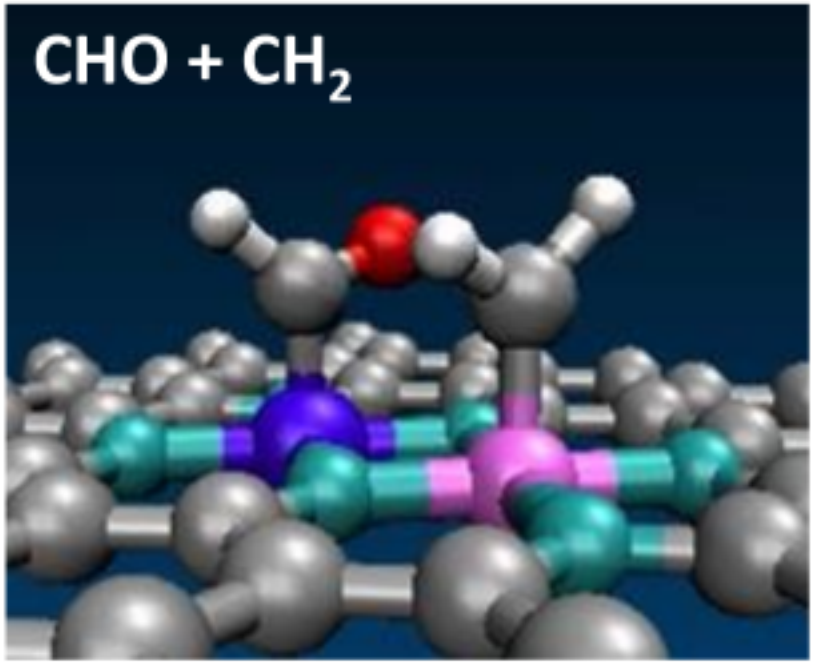

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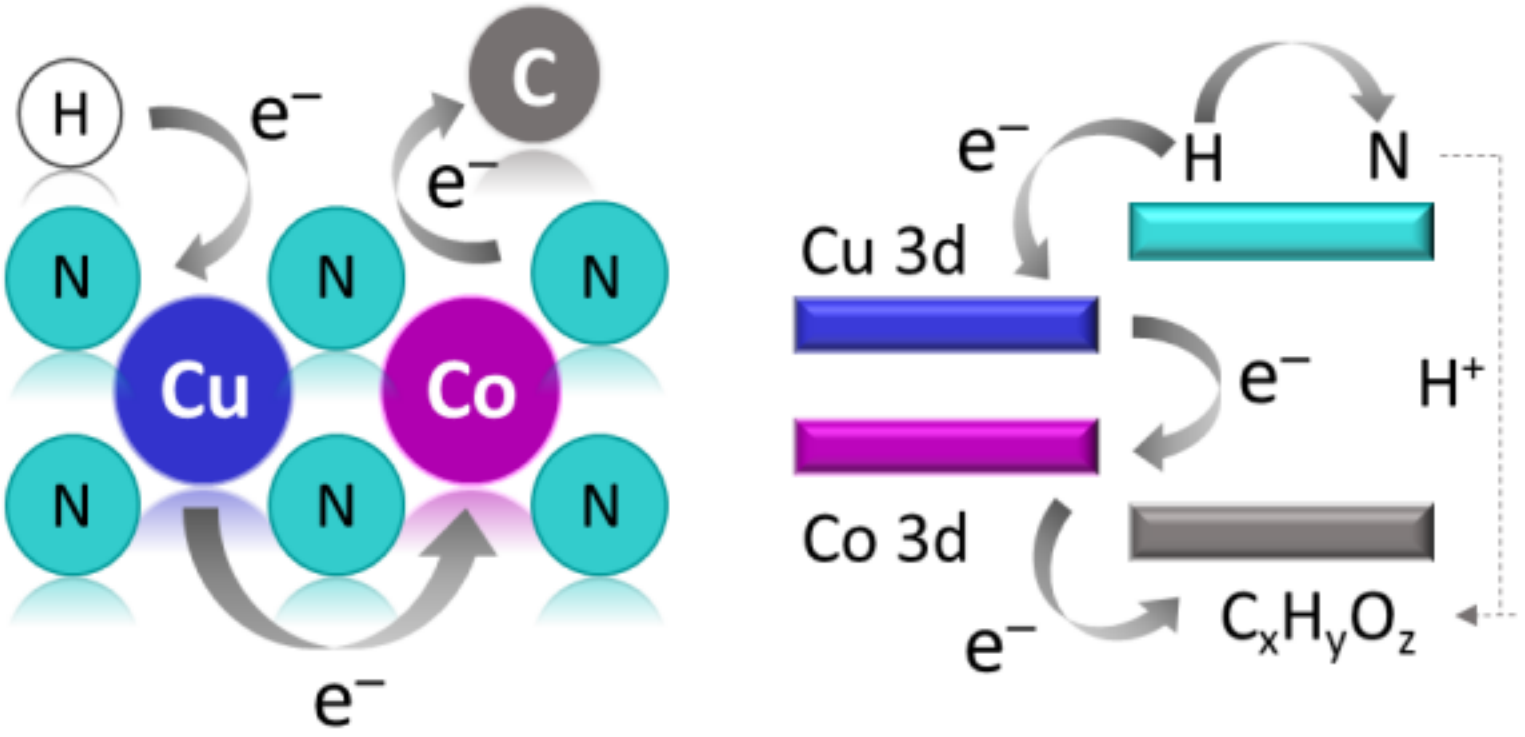
Suggested reduction cycle



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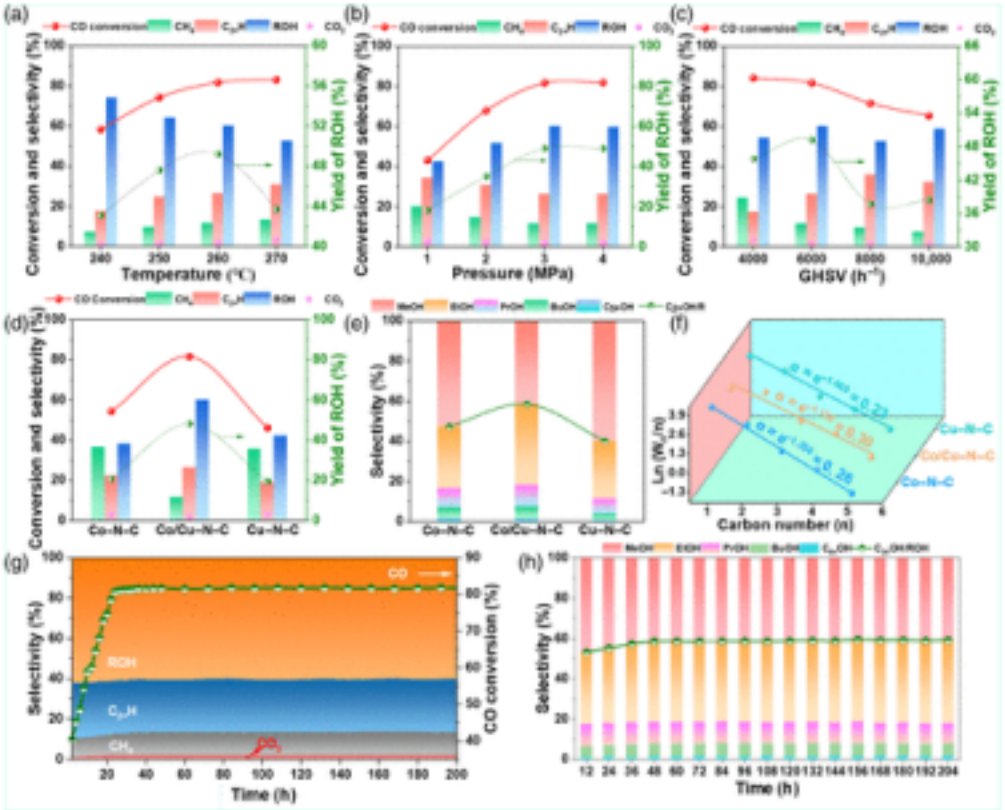
Catalytic performance



- CO conversion 81.7%
- Selectivity 58.5%
- STY 851.58 mg/(g··h)
- GHSV 6000 h^{-1}

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Conclusions

1. Theory can be efficiently used for the rational design of hybrid catalytic materials for reduction reactions;
2. Particularly, a targeted change of band alignment, work-function, charge localization and density-of-states is possible to enhance the catalytic performance;
3. This type of theoretical research contributes to bridge the so called “materials gap” between theory and experiment.

Acknowledgements

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Prof. Shuliang Yang

M.A. Syzgantseva

All co-authors

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SB-RAS supercomputer center

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