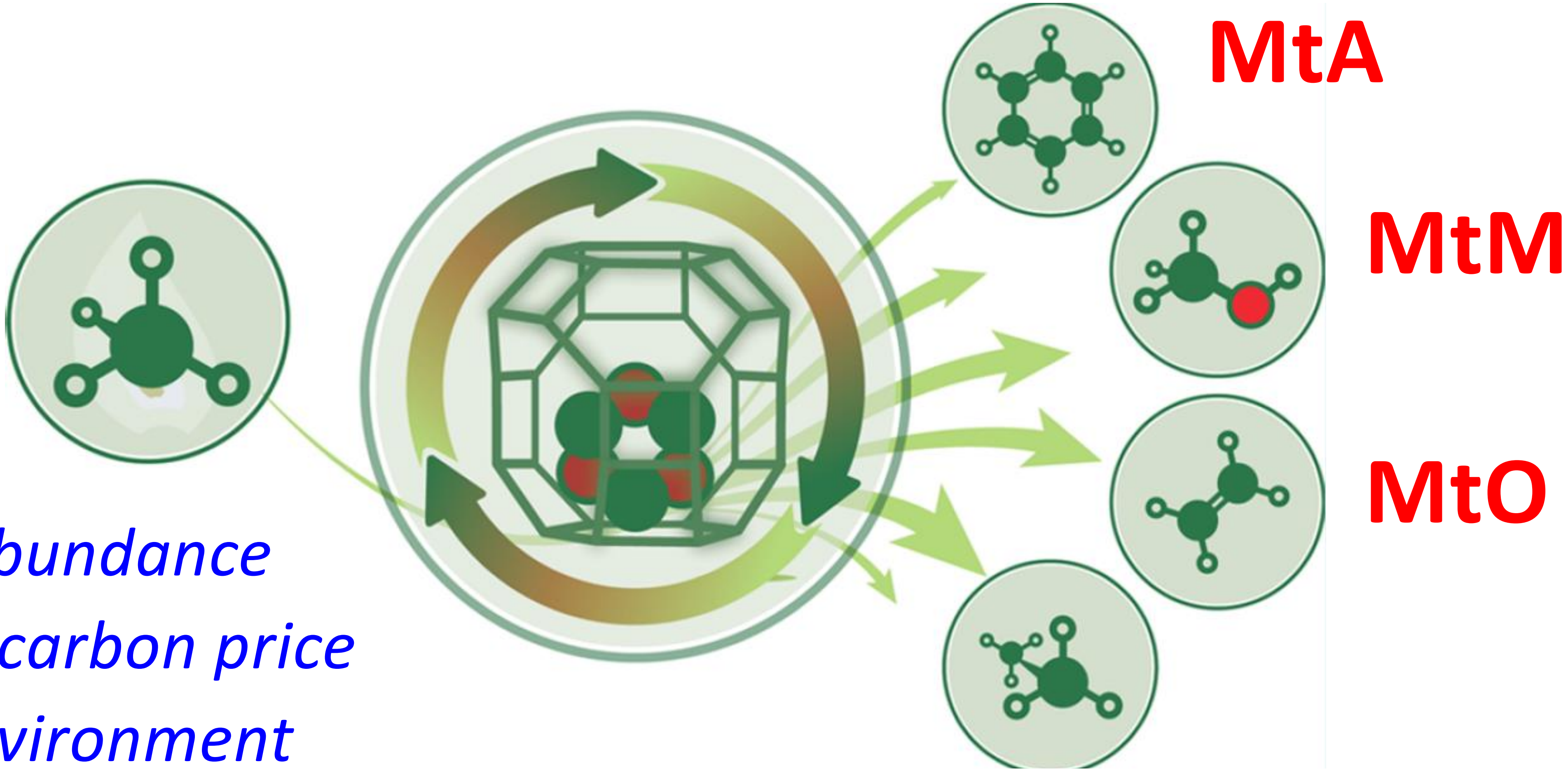
Methane conversion to methanol over copper-exchanged zeolites: molecular understanding of the process using *in situ* physical chemical methods

Vitaly L. Sushkevich

Paul Scherrer Institute, ETH Zurich

Some slides: courtesy of M. Artsiusheuski, A. Brenig and J. Fischer

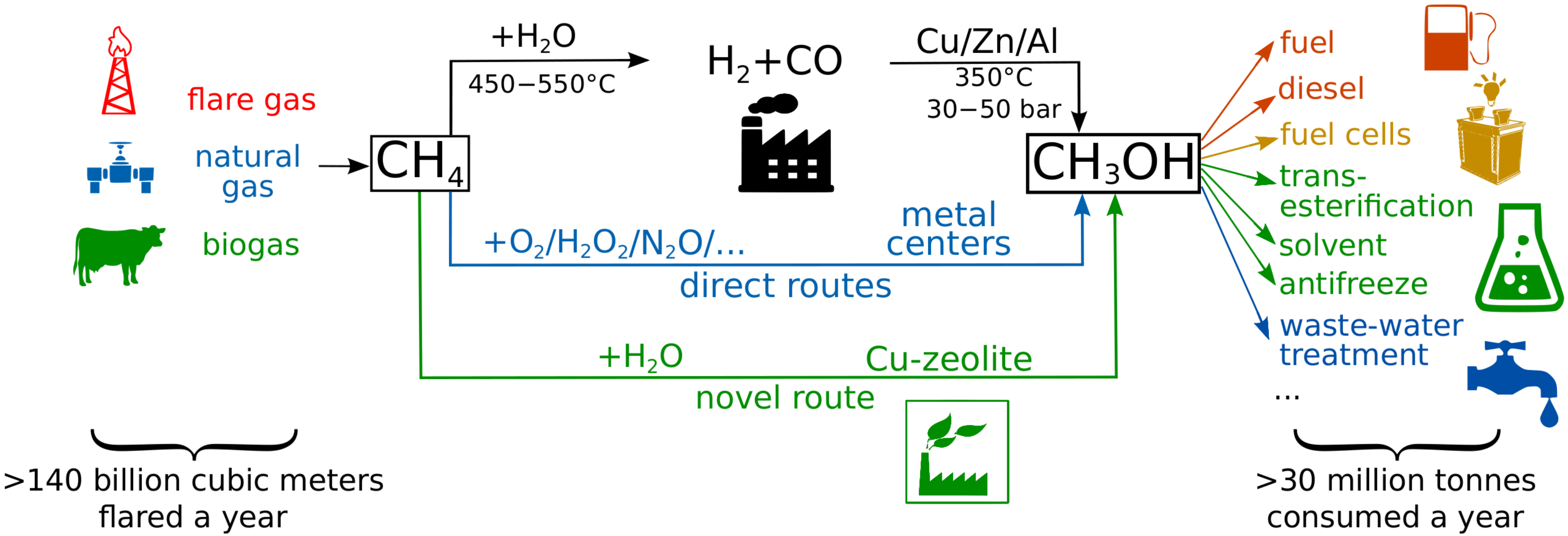
Routes for methane valorization



- *Abundance*
- *Low carbon price*
- *Environment*

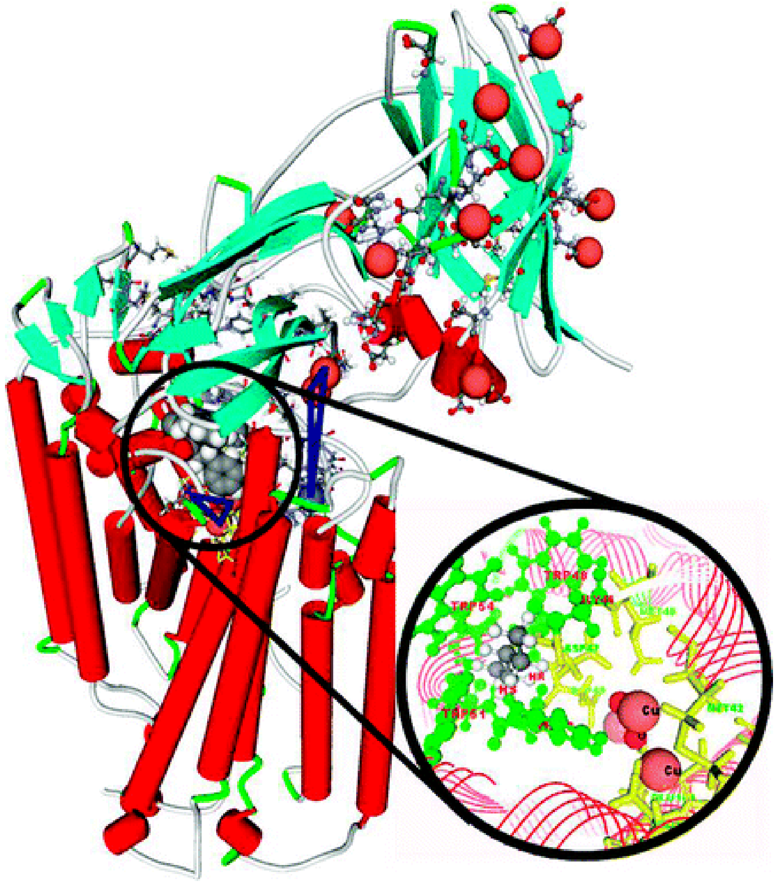
A. Olivos-Suarez et al, ACS Catal., 2016, 6, 2965-2981

Routes for methane conversion into methanol

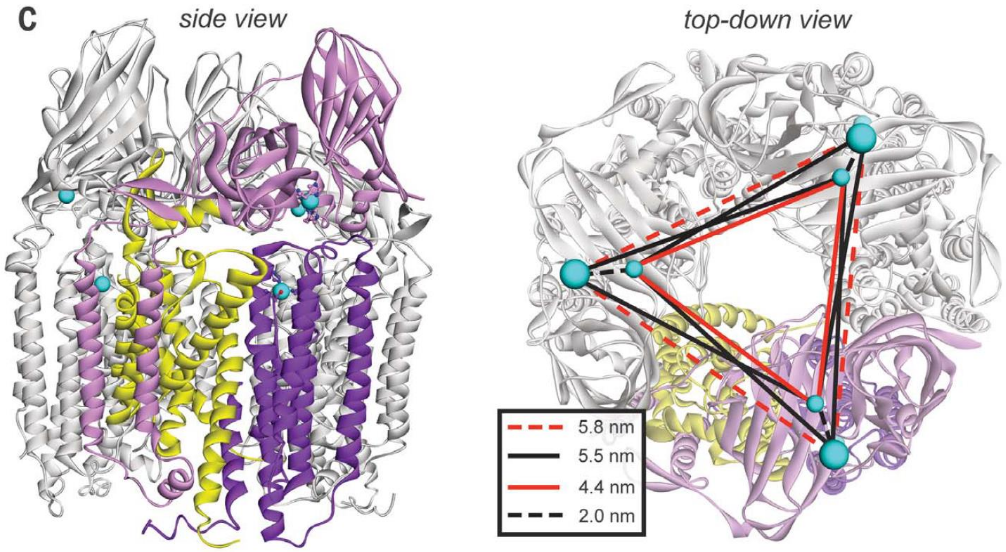


V. Sushkevich et al., *Science*, 2017, 356, 523

Particulate methane monooxygenase



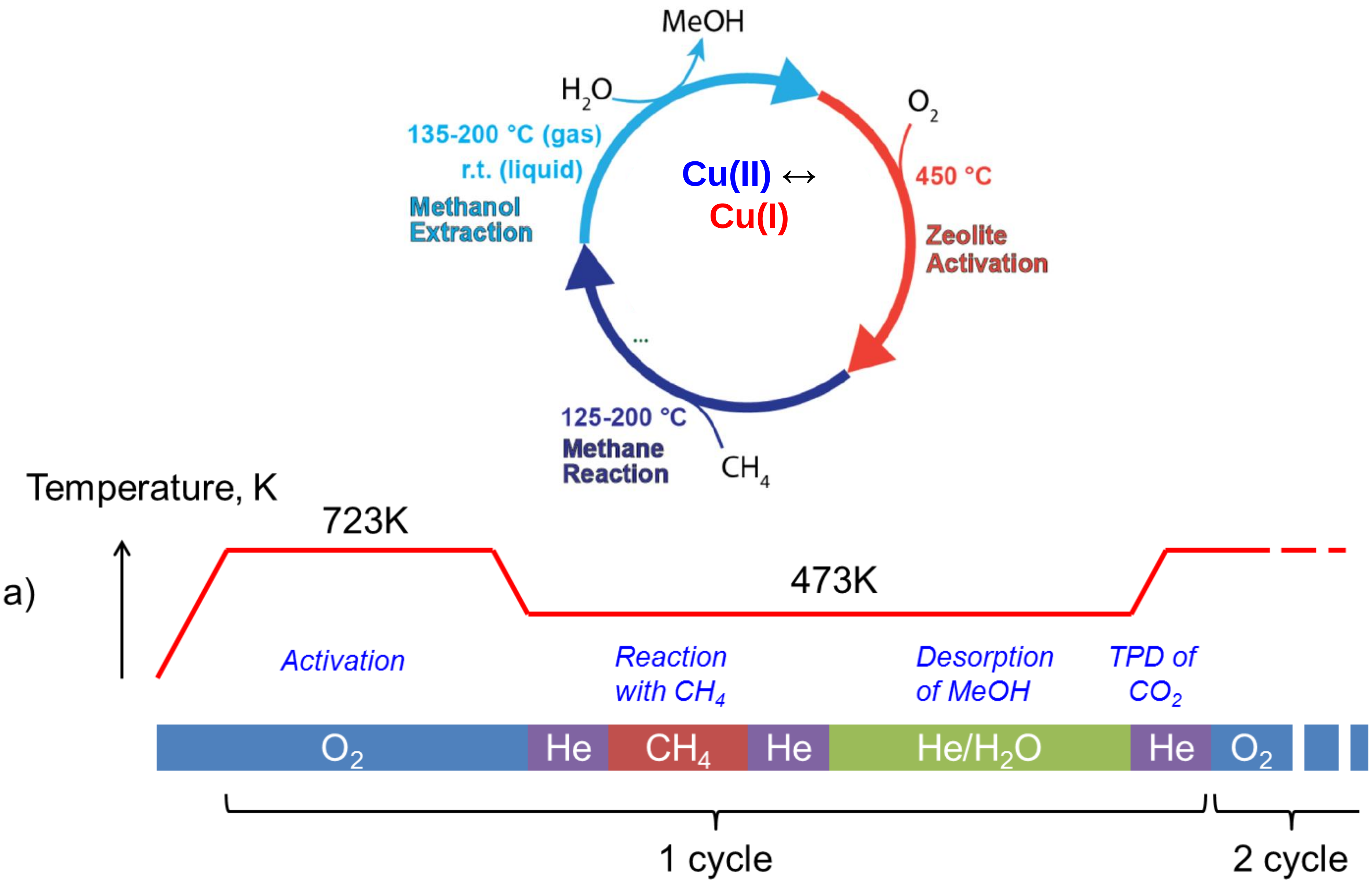
S. I. Chan, S. S. F. Yu, *Acc. Chem. Res.* **41**, 969 (2008)



Ross et al., *Science* **364**, 566 (2019)

… different structures of copper sites are suggested ranging from copper monomers to copper trimers…

Methanol synthesis via chemical looping



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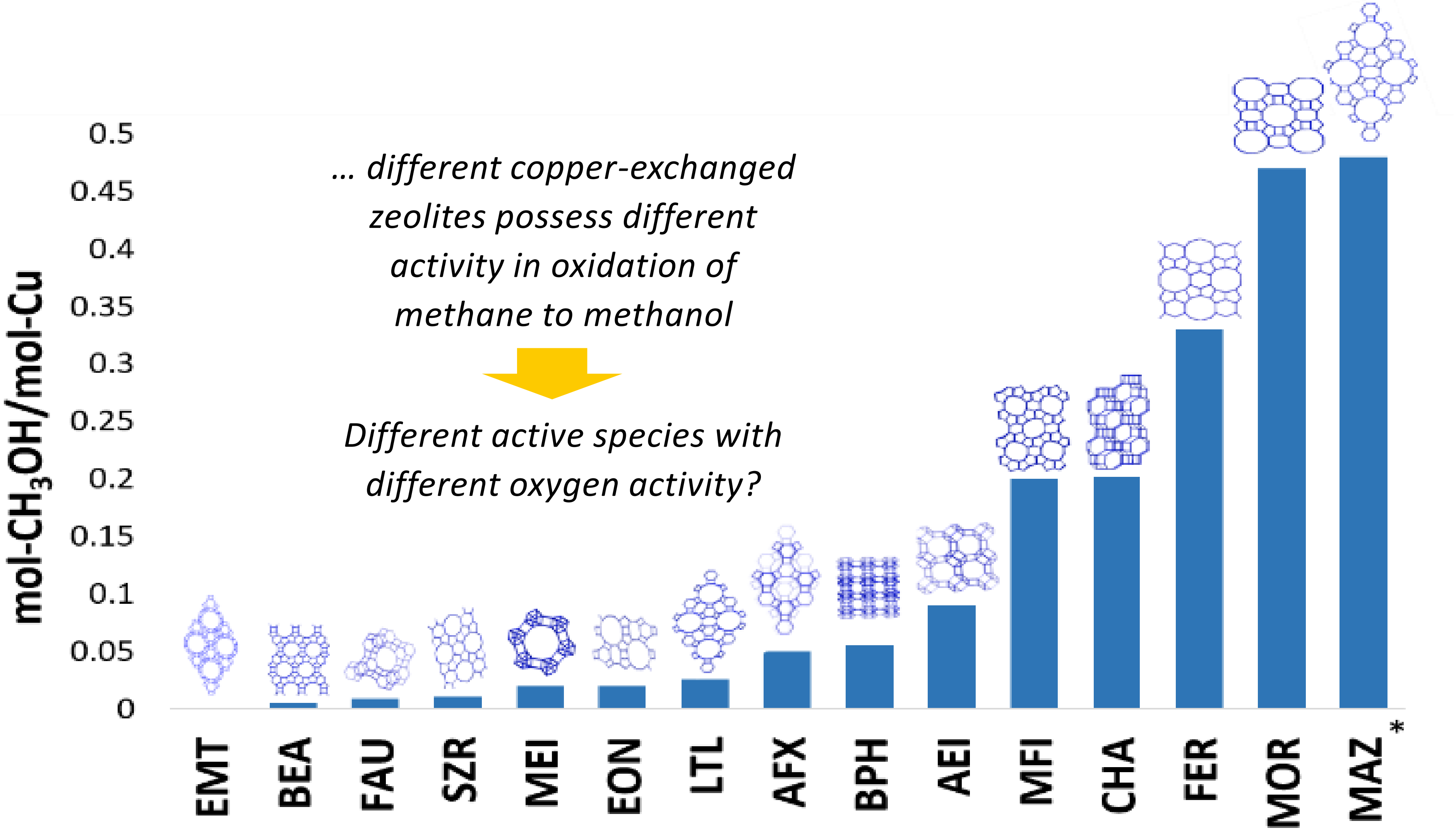
Copper-exchanged zeolites – perspective materials for the methane conversion to methanol

… different copper-exchanged zeolites possess different activity in oxidation of methane to methanol

Different active species with different oxygen activity?



M. Newton et al, Chem. Soc. Rev., 2020

In situ and operando study of direct methane conversion to methanol

$CH_4 \rightarrow CH_3OH$

In situ

Active sites

- XAS study of Cu species
- Reducibility assessment using in situ CH_4-TPR
- Oxygen isotope exchange

Fate of methane

- MAS NMR and FTIR identify reaction products
- Effect of zeolite topology on the product distribution
- Mechanism of HC formation

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Site-specific kinetics

- Operando UV-vis powered by in situ EPR
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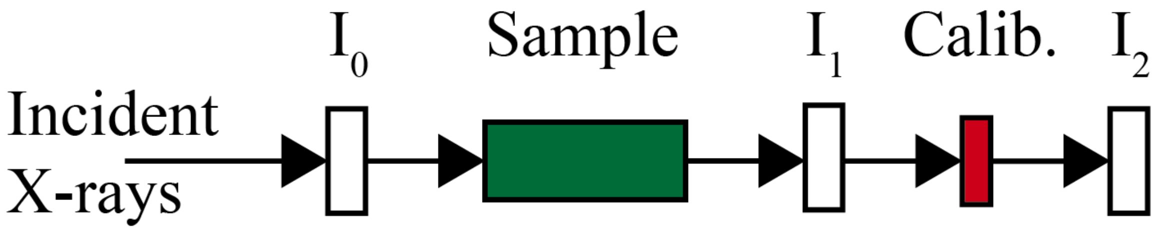
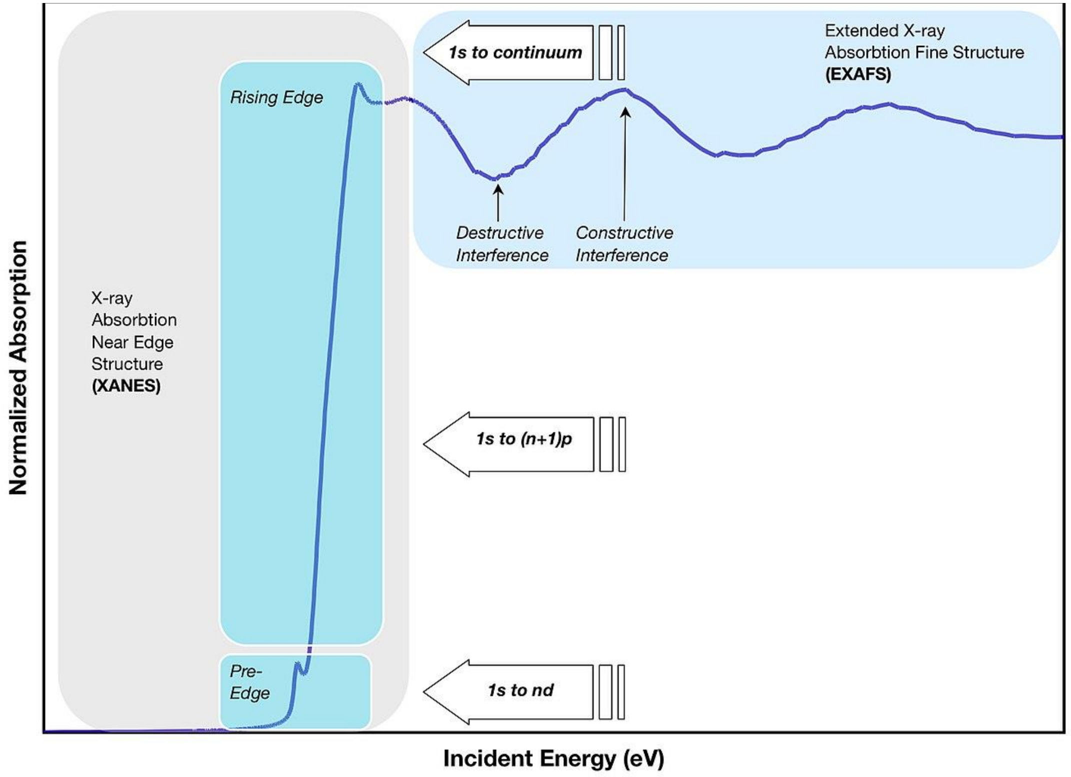
XAS Spectroscopy

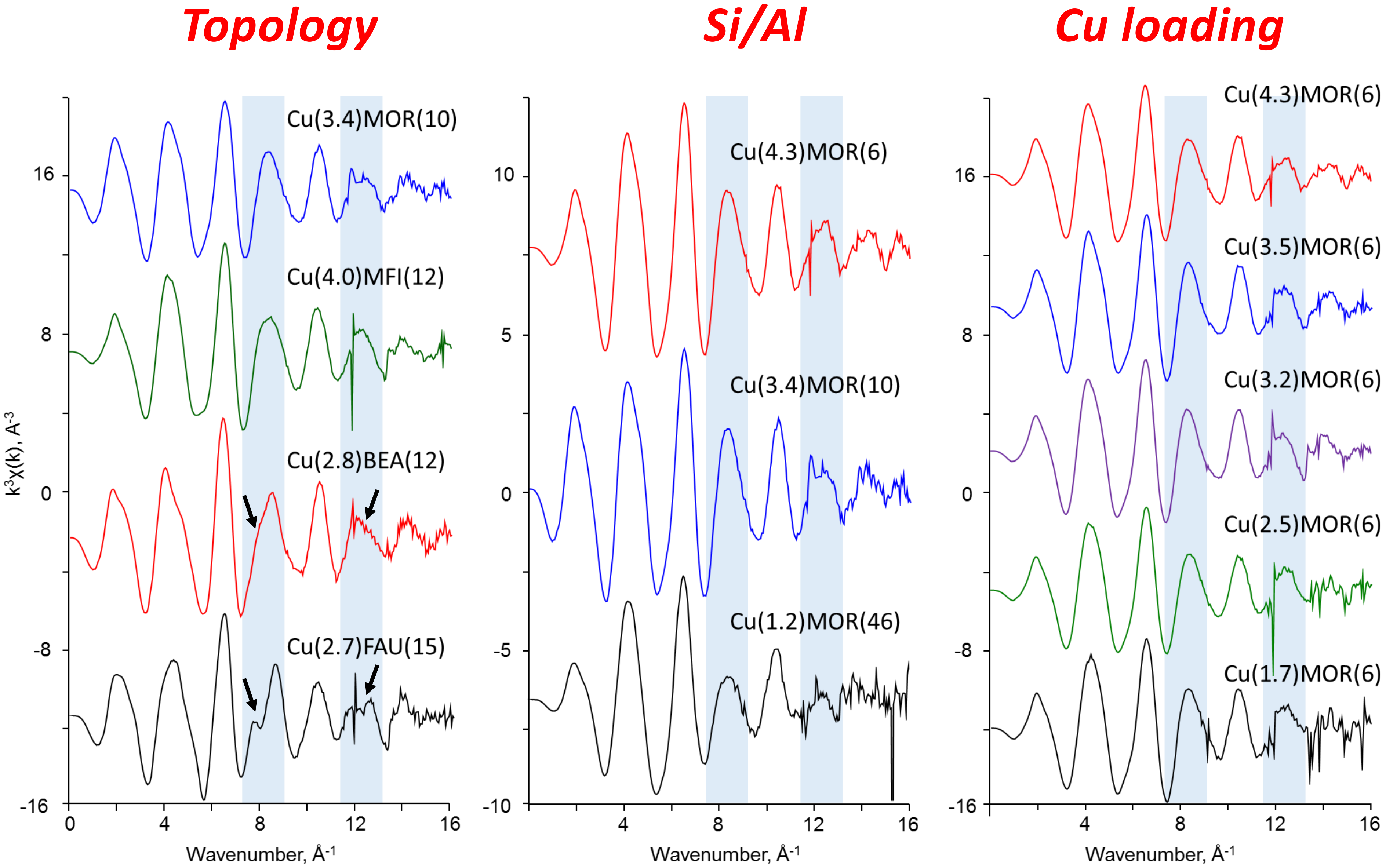
- Measurement of the absorption coefficient across the energy in transmission geometry





- XANES: X-ray Absorption Near Edge Structure
  - Valence state
  - Energy bandwidth
  - Bond angles
- EXAFS: Extended X-ray Absorption Fine Structure
  - **Interatomic distances**
  - **Near neighbor coordination numbers**
  - Lattice dynamics

Analyzing copper species using EXAFS



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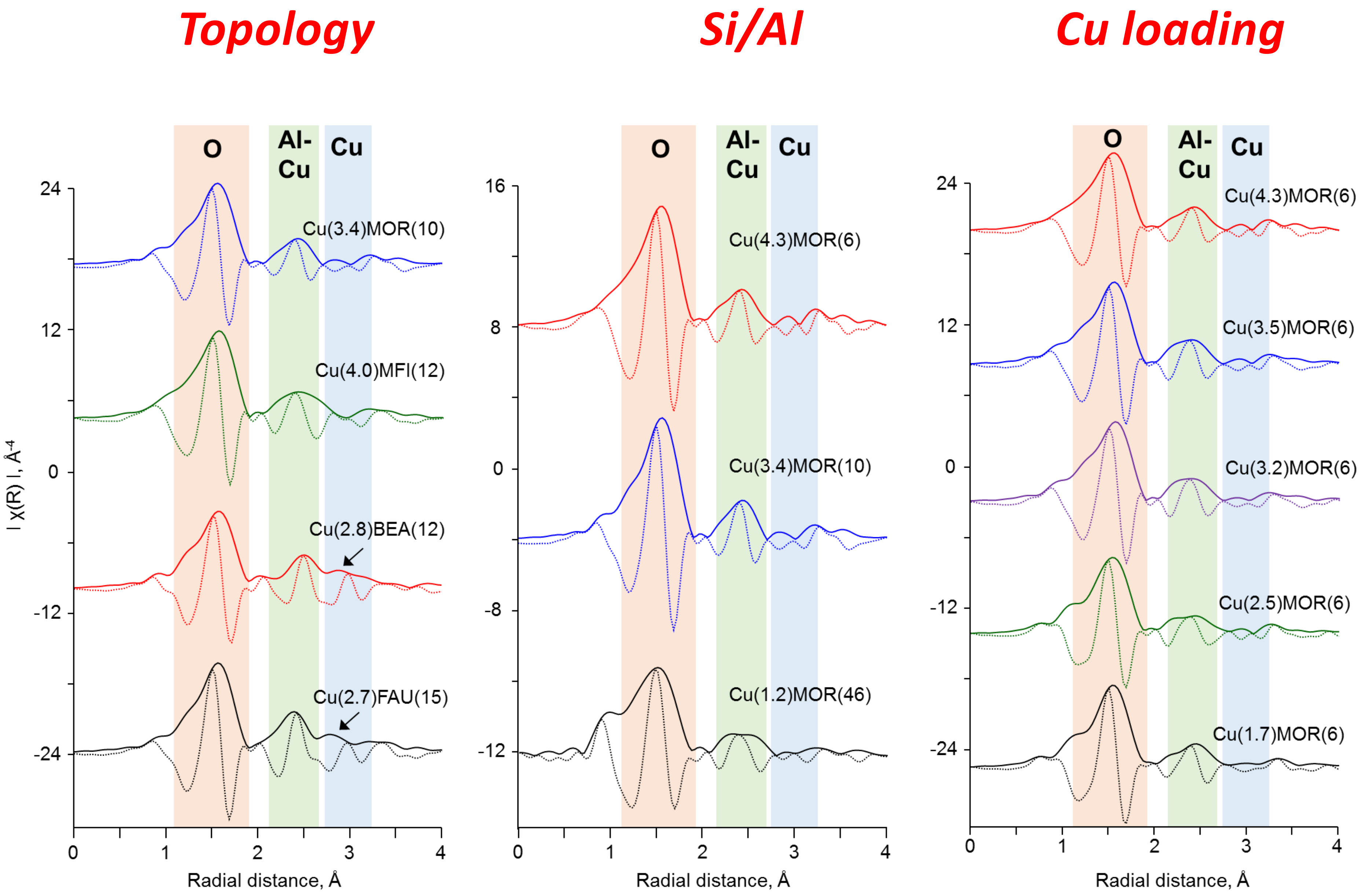
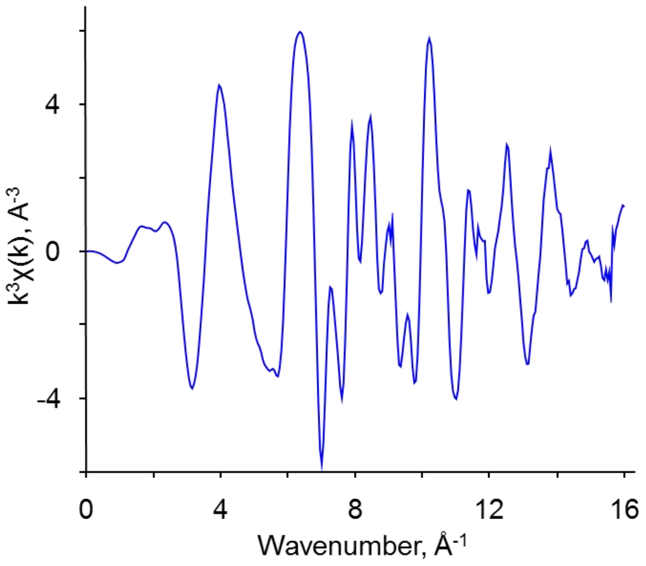
Analyzing copper species using FT EXAFS

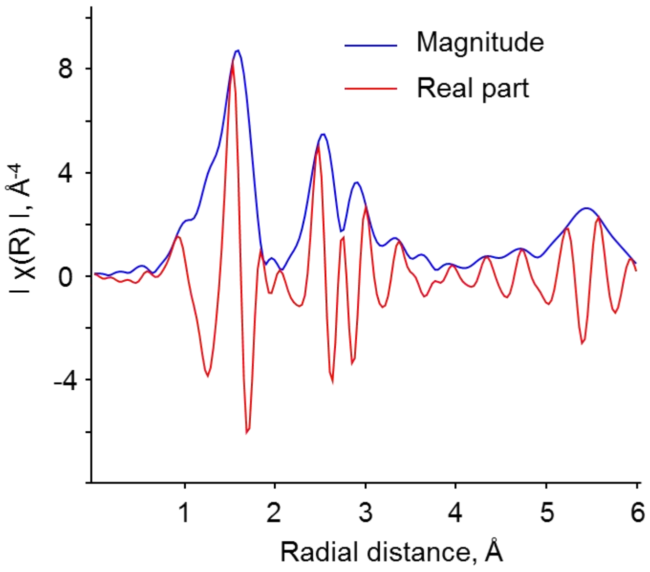


Analyzing copper species using wavelet EXAFS

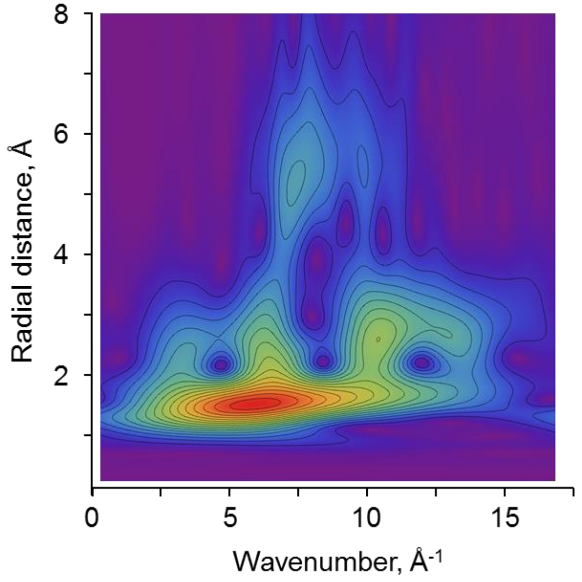
k^3-EXAFS

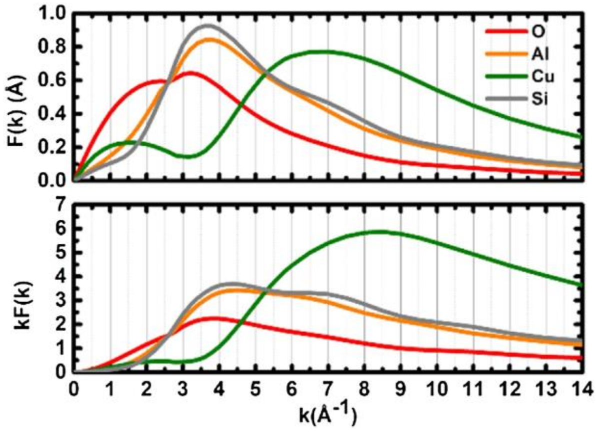


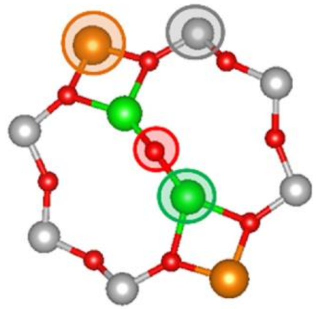
FT EXAFS



WT EXAFS







Sushkevich et al., Chem. Sci., 2020, 11, 5299

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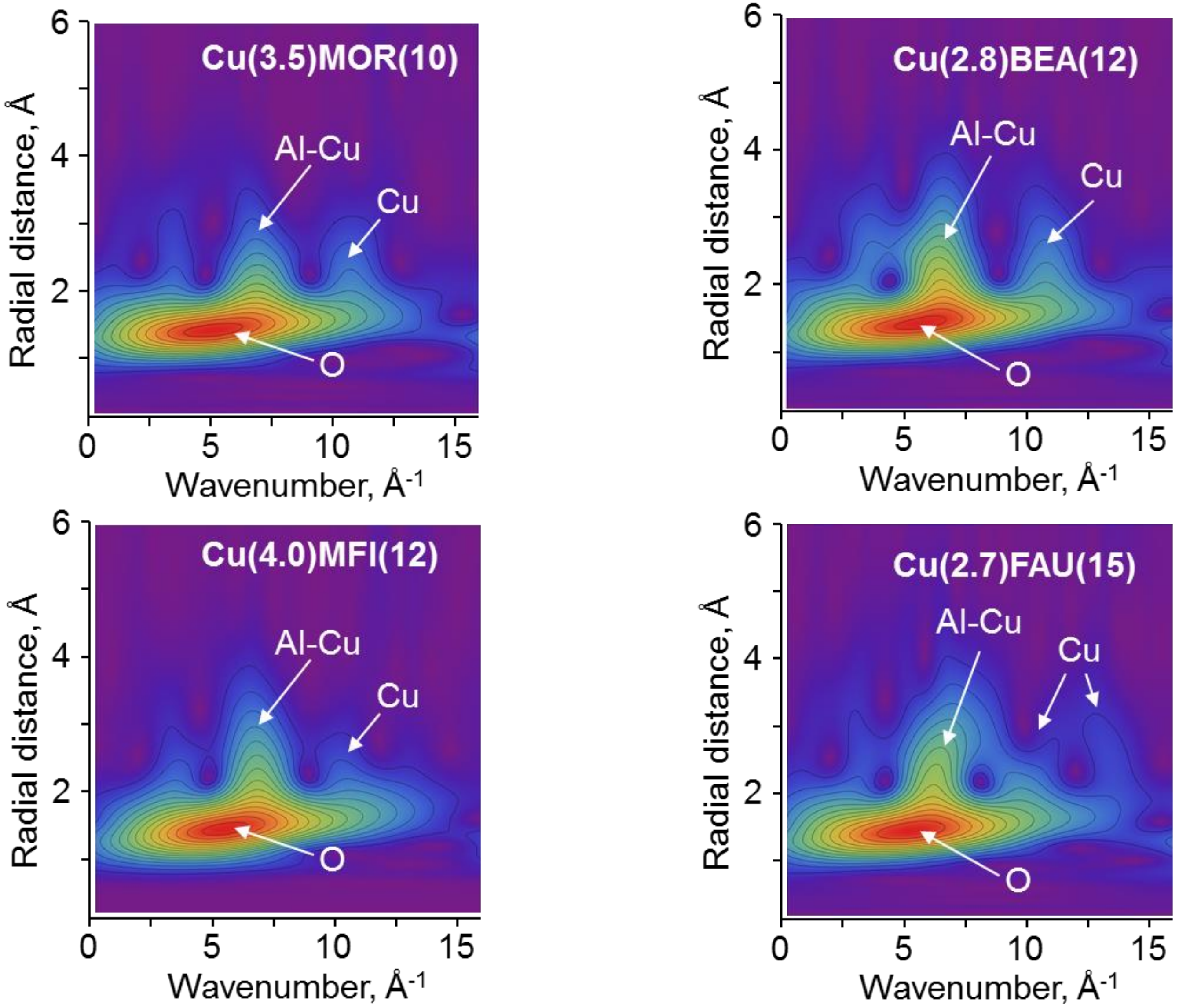
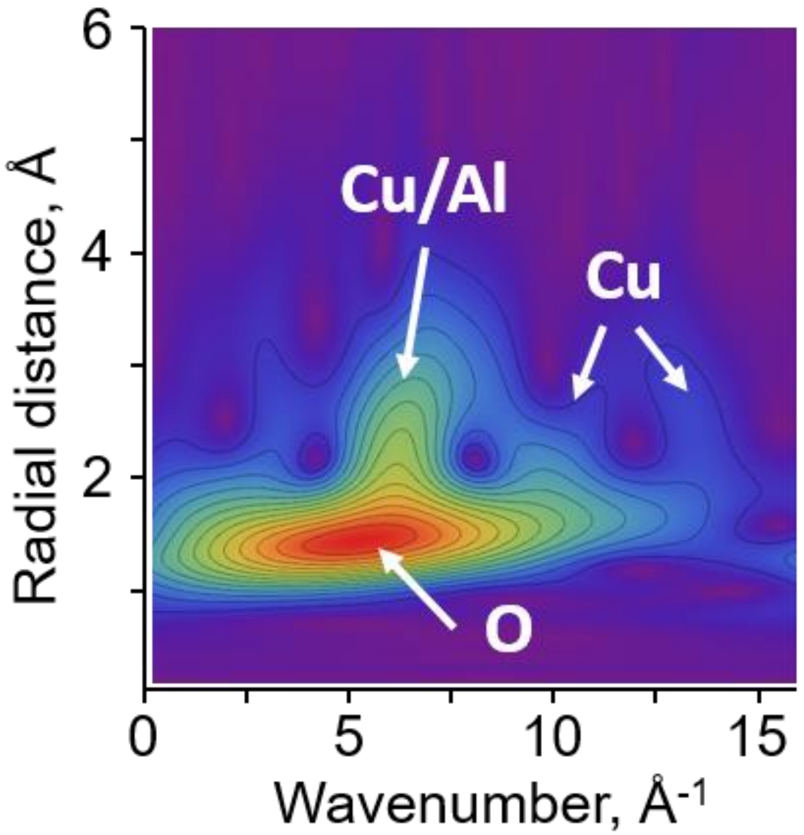
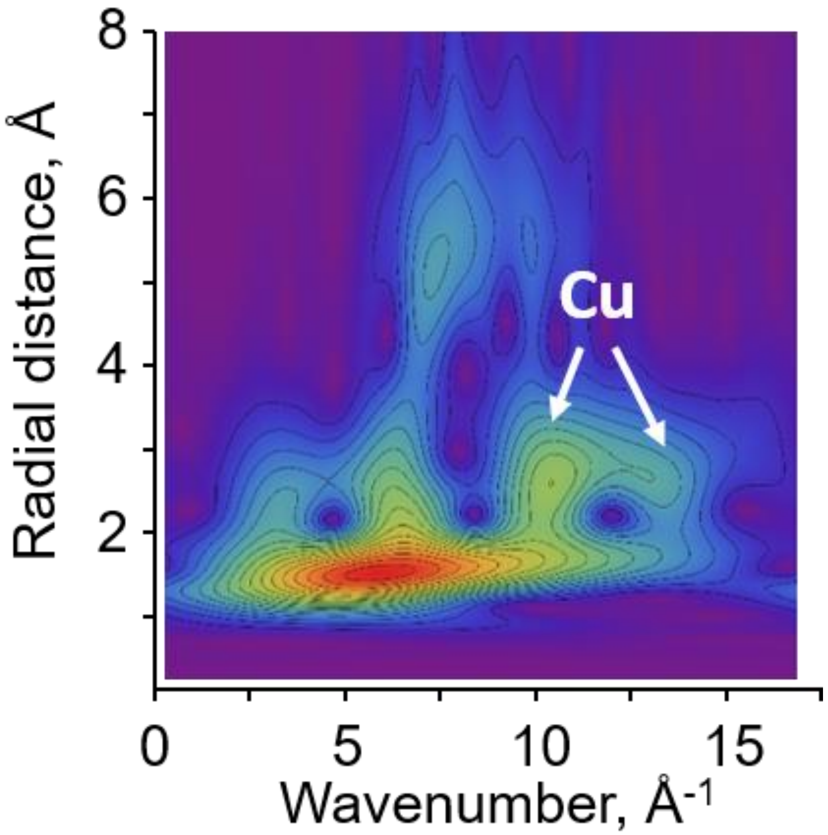


Analyzing copper species using wavelet EXAFS

Cu(2.8)FAU(15)



Copper (II) oxide



Clustering of copper in faujasite

Sushkevich et al., Chem. Sci., 2020, 11, 5299

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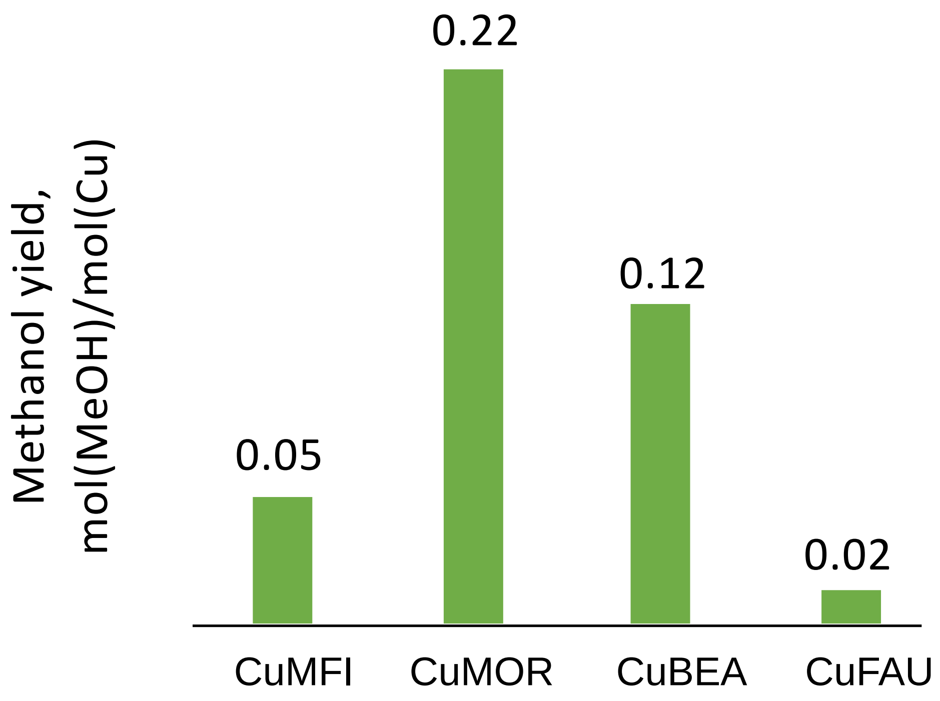
Achievement of high methanol yield

Different topologies with similar Si/Al and Cu loading:

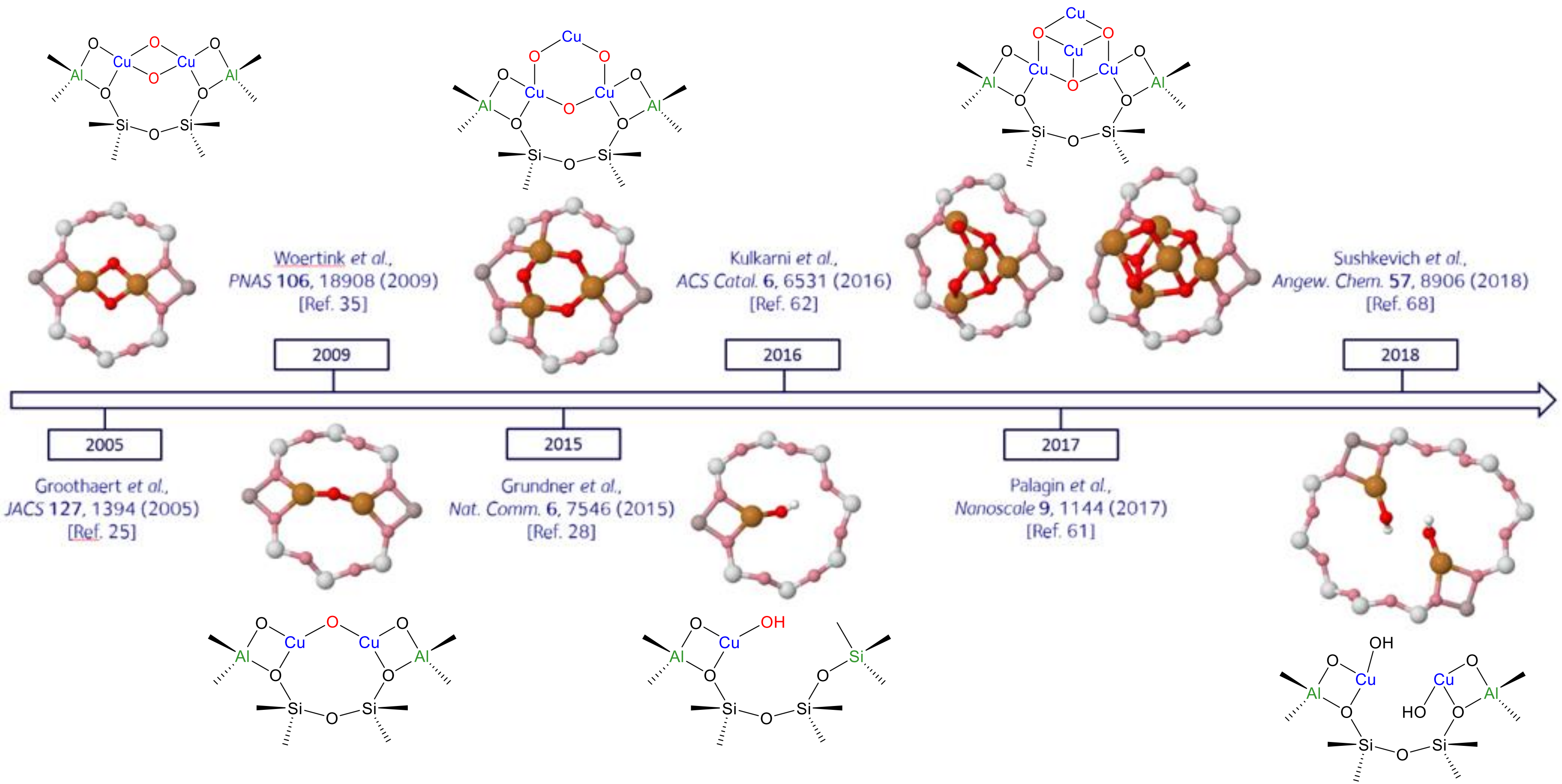
Si/Al = 10-15

Copper loading 3-4 wt%



activation: O_2, 673 K, 1 h; reaction CH_4 7 bar at 473 K

Achievement of high methanol yield



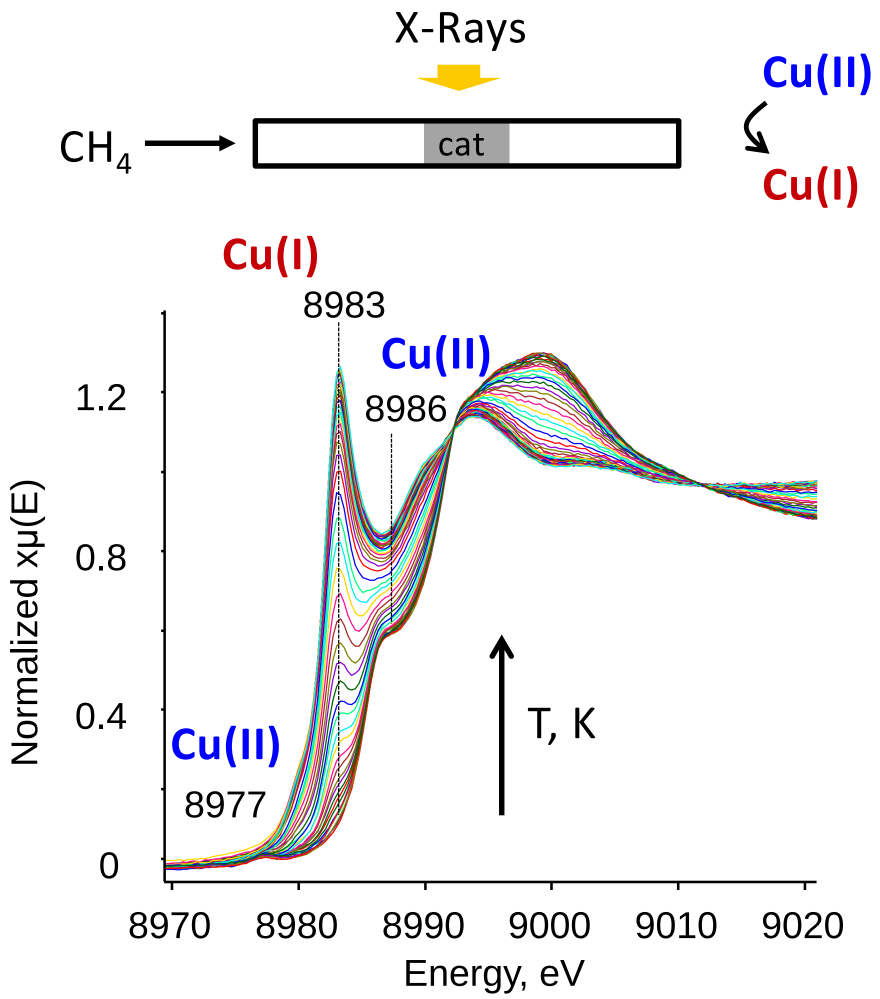
A priori different reducibility and oxygen lability:

but how to study experimentally?

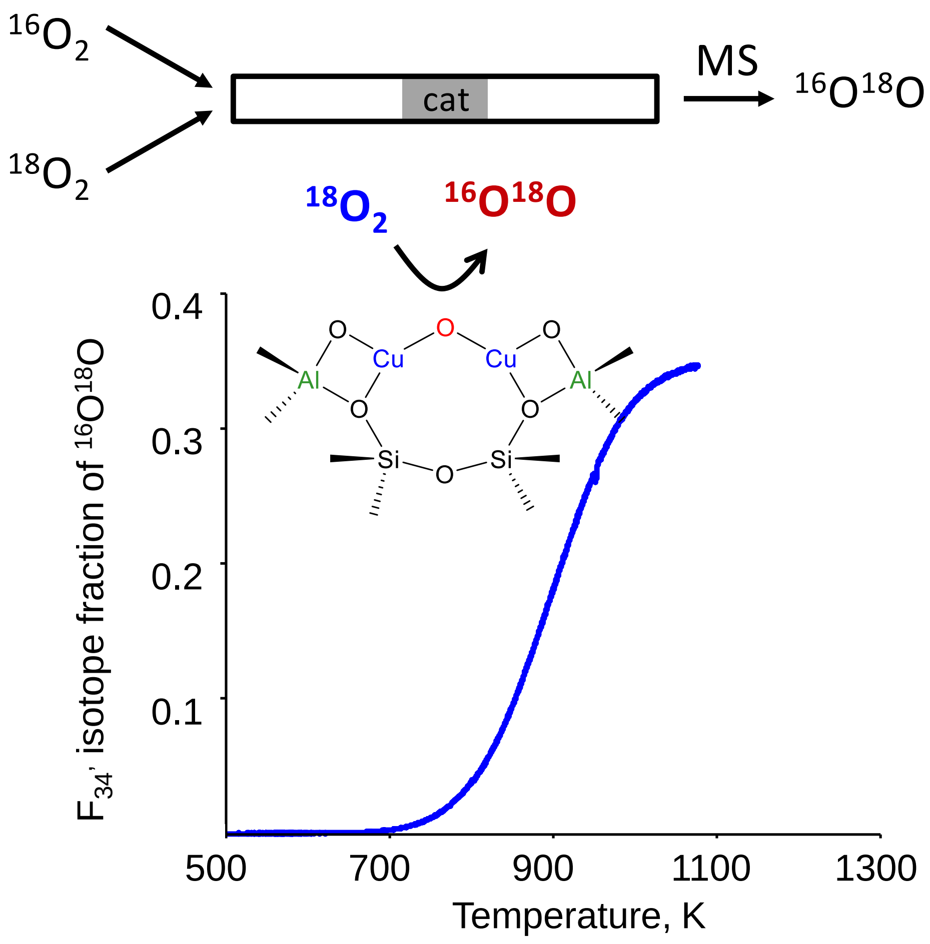
M. Newton et al, Chem. Soc. Rev., 2020, 49, 1449

Reducibility of copper species and oxygen lability

Temperature-programmed reaction with methane



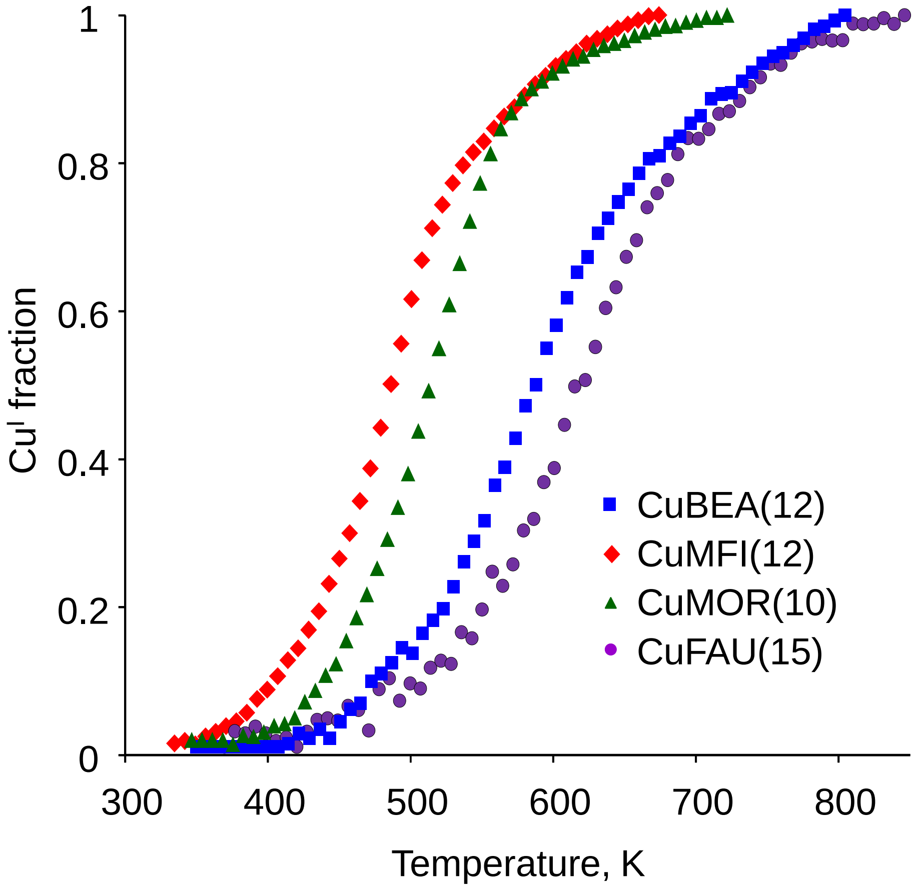
Temperature-programmed $^{16}O_2$-$^{18}O_2$ isotope exchange



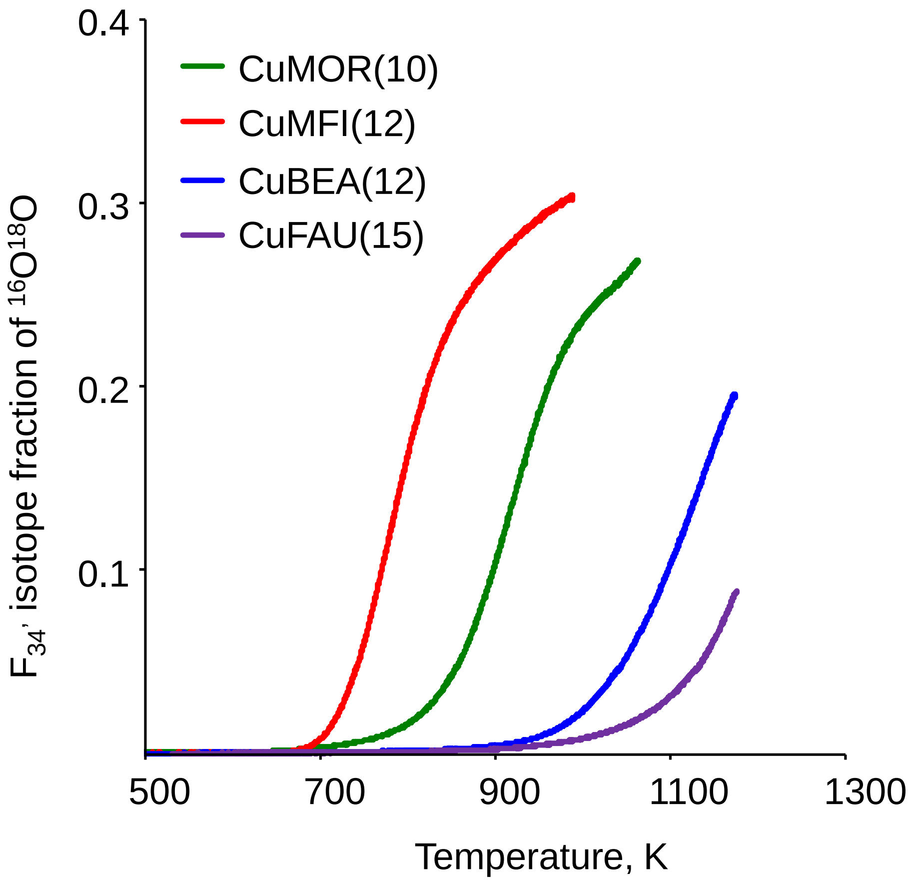
Sushkevich and van Bokhoven, ACS Catal., 2019, 9, 6293

Reducibility of copper species hosted in zeolite of different topology

TPR-CH_4-XANES

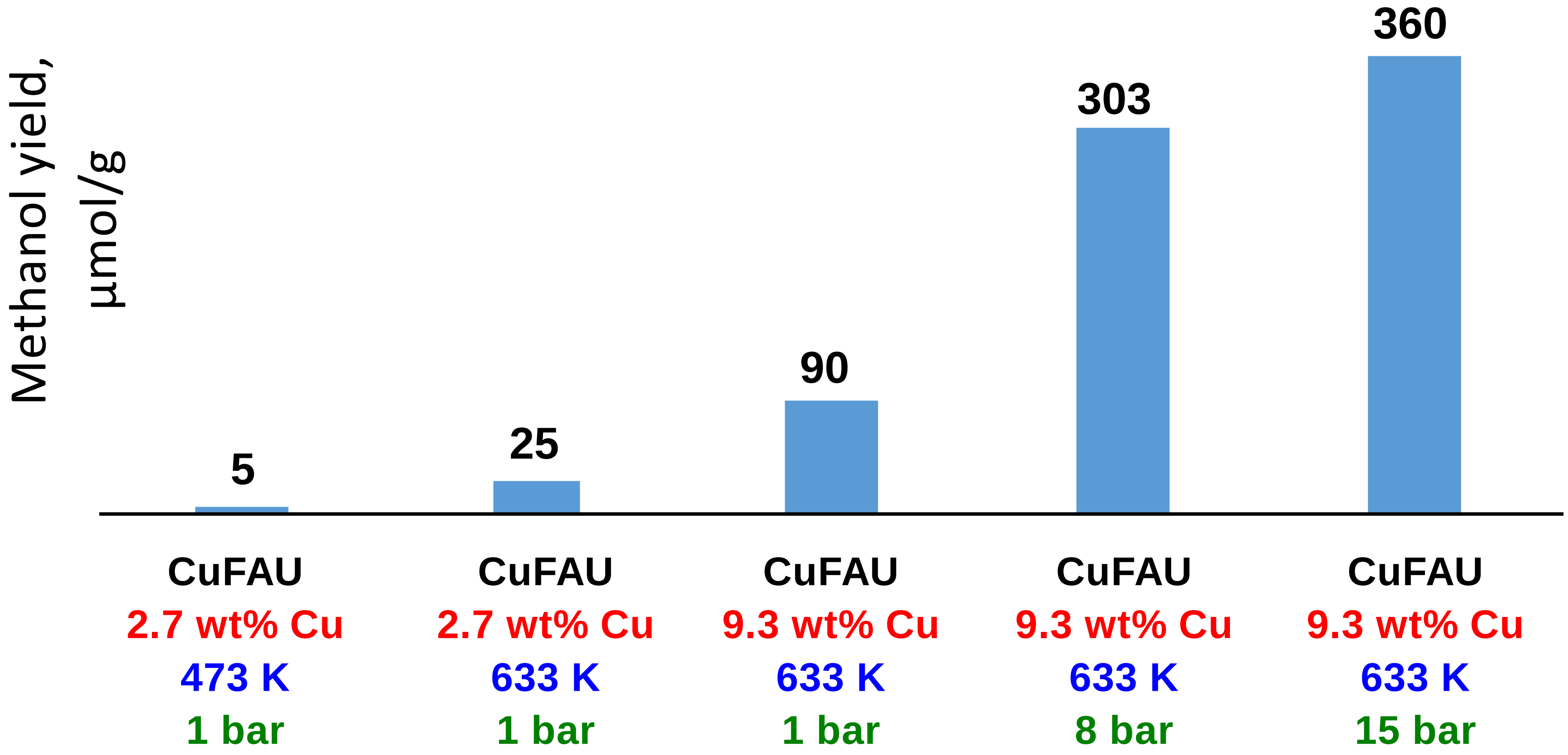


$^{16-18}O_2$ oxygen exchange



Sushkevich and van Bokhoven, ACS Catal., 2019, 9, 6293

Achievement of high methanol yield



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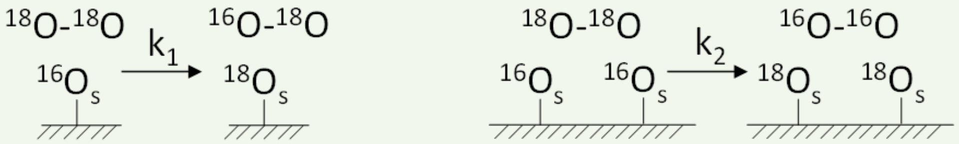
Oxygen isotope exchange in CuMOR

Experimental setup

Kinetic model

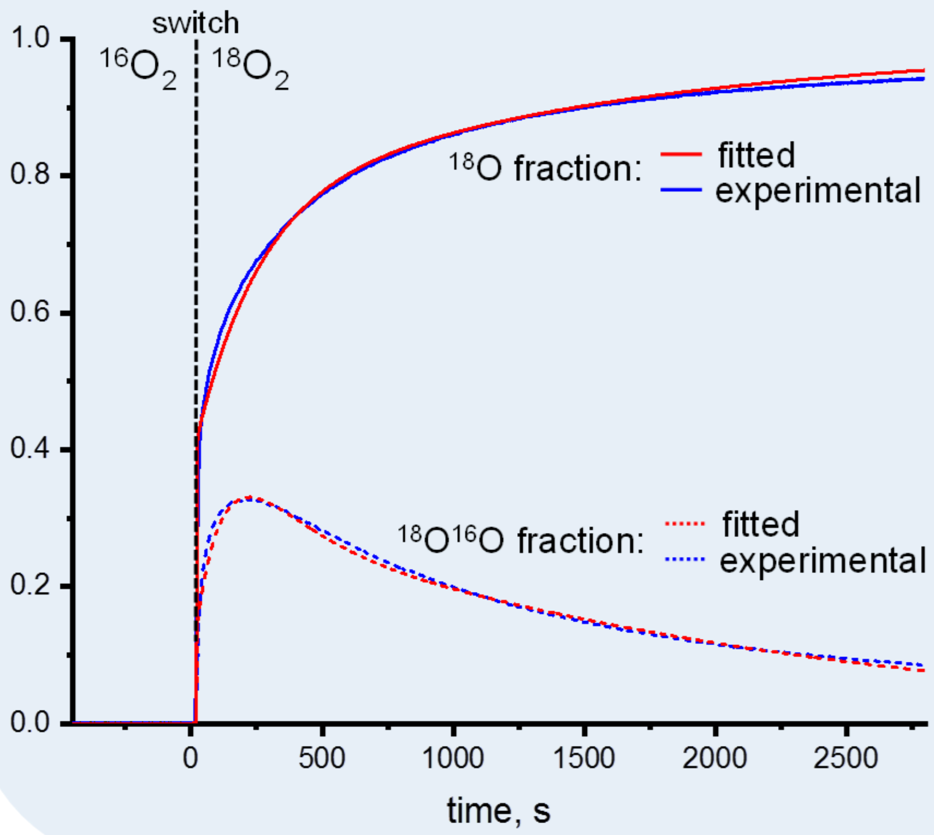
single-atom (***R***[1]) type   two-atom (***R***[2]) type



- 2 kinetically different sources of exchangeable oxygen atoms
- for each source ***R***[1] and ***R***[2] exchange mechanisms are possible
- $$\frac{\partial x_i(t,l)}{\partial t} = -\frac{1}{\tau}\frac{\partial x_i(t,l)}{\partial l} - \sum_{\substack{i=32,34,36\ m/z \\ j=1,2}} f(cj, xi, k_{1j}, k_{2j})$$

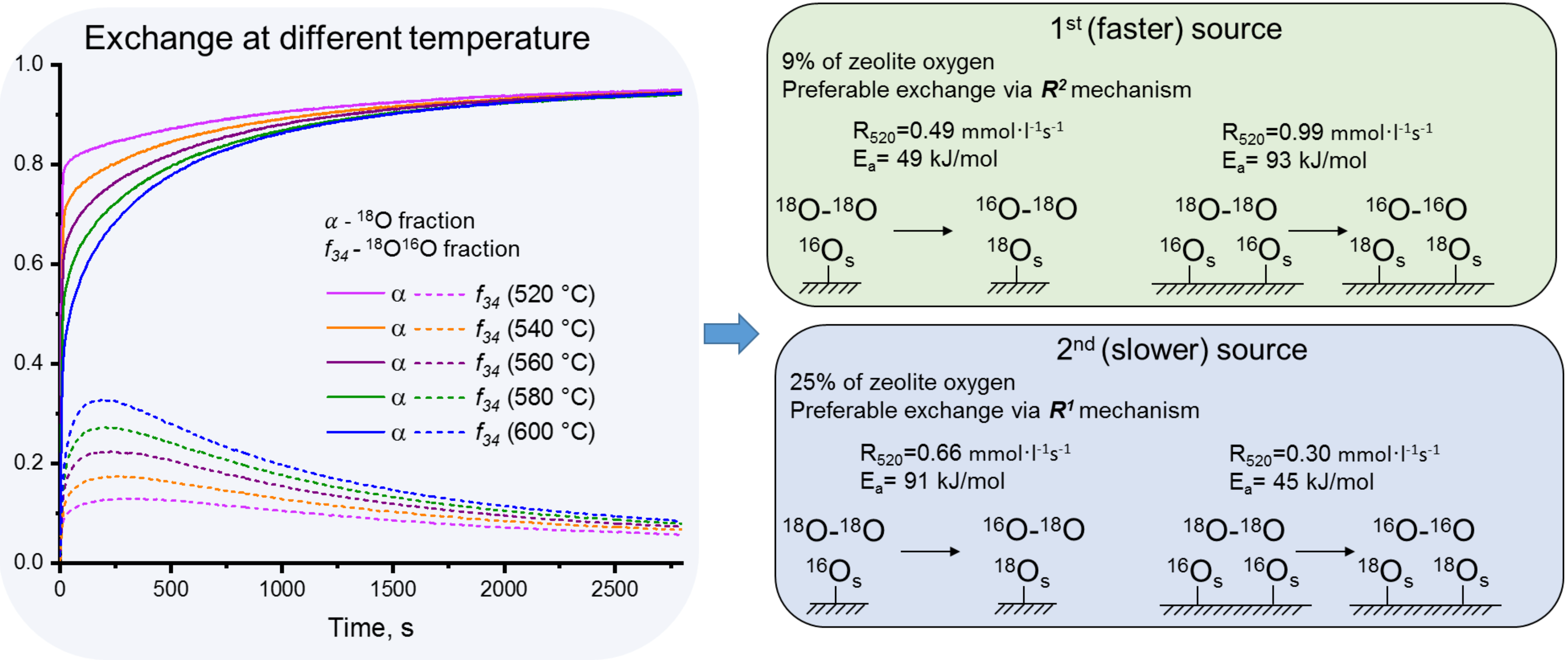
Flow term   Kinetic term

Model verification



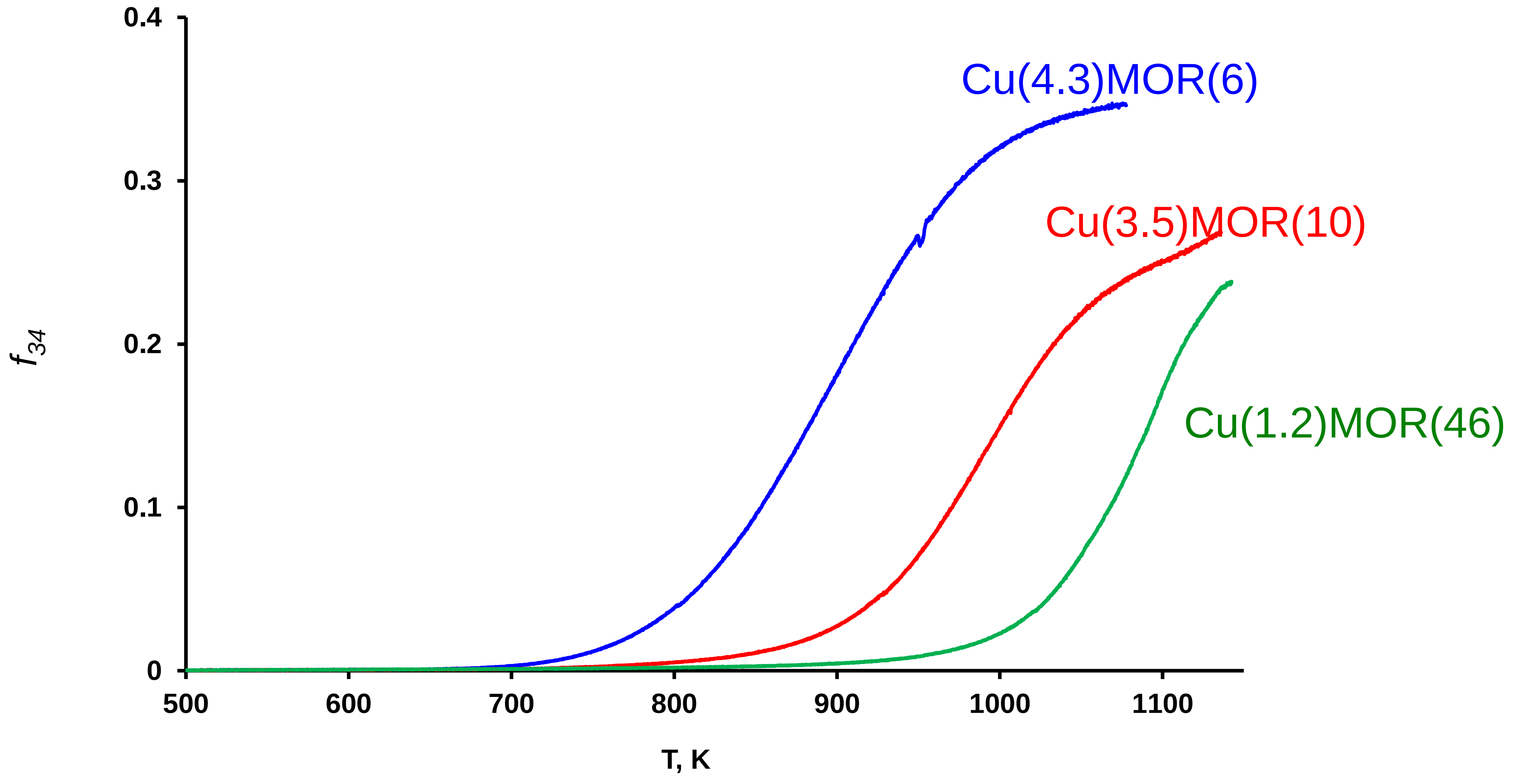
Artsiusheuski et al., JPCC, 2021, 125, 12366

Oxygen isotope exchange in CuMOR



- *Linking the kinetic parameters and activation energies to the structure of copper species, hosted in different zeolites*
- *Effect of copper loading, Si/Al, topology, co-cation, etc.*

Effect of Si/Al ratio: temperature-programmed isotope exchange

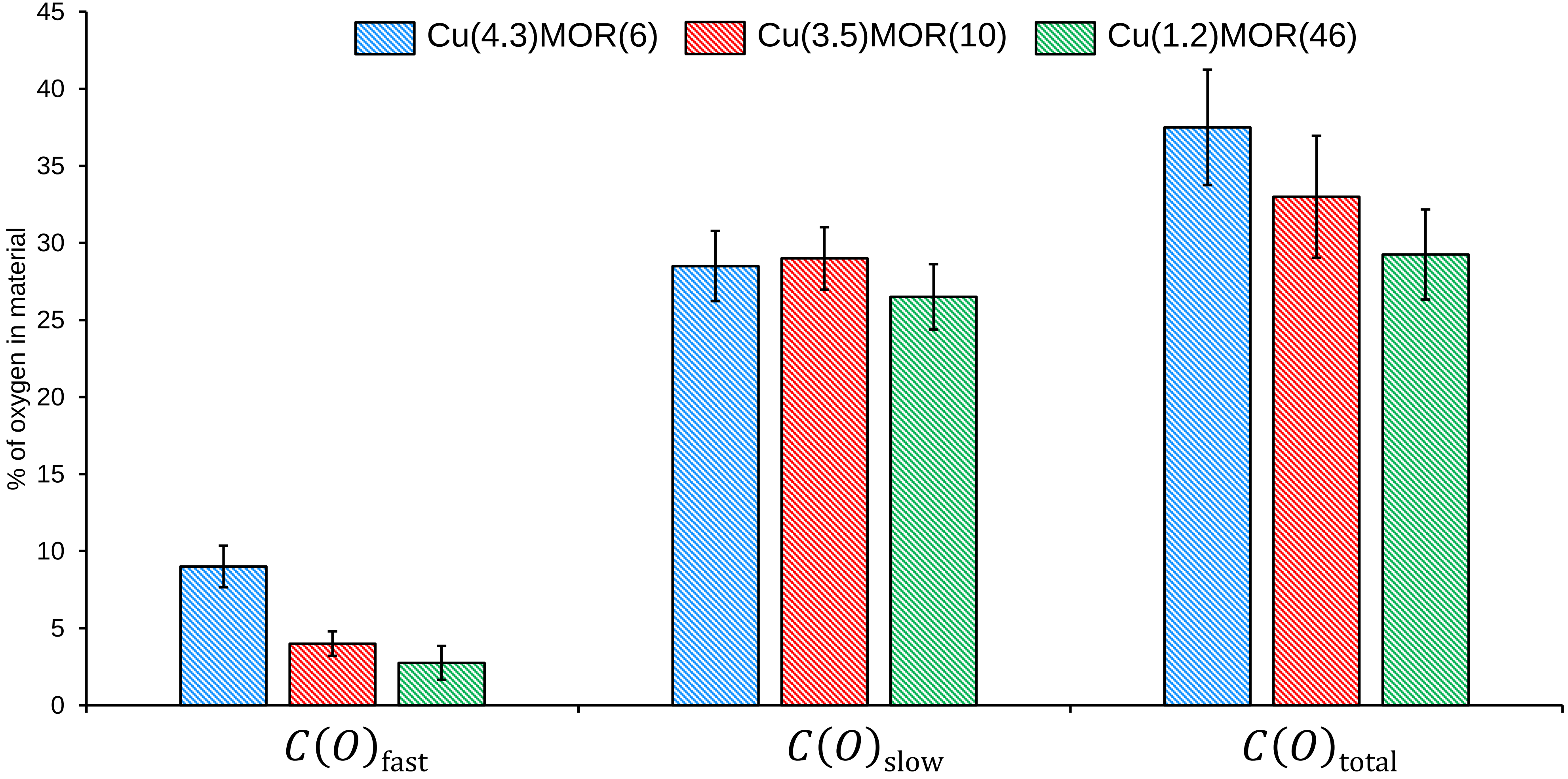


- Si/Al ratio significantly effects the rate of exchange
- Isothermal experiments are possible only in different temperature ranges => cannot compare *k*

However, can compare *C(O)*

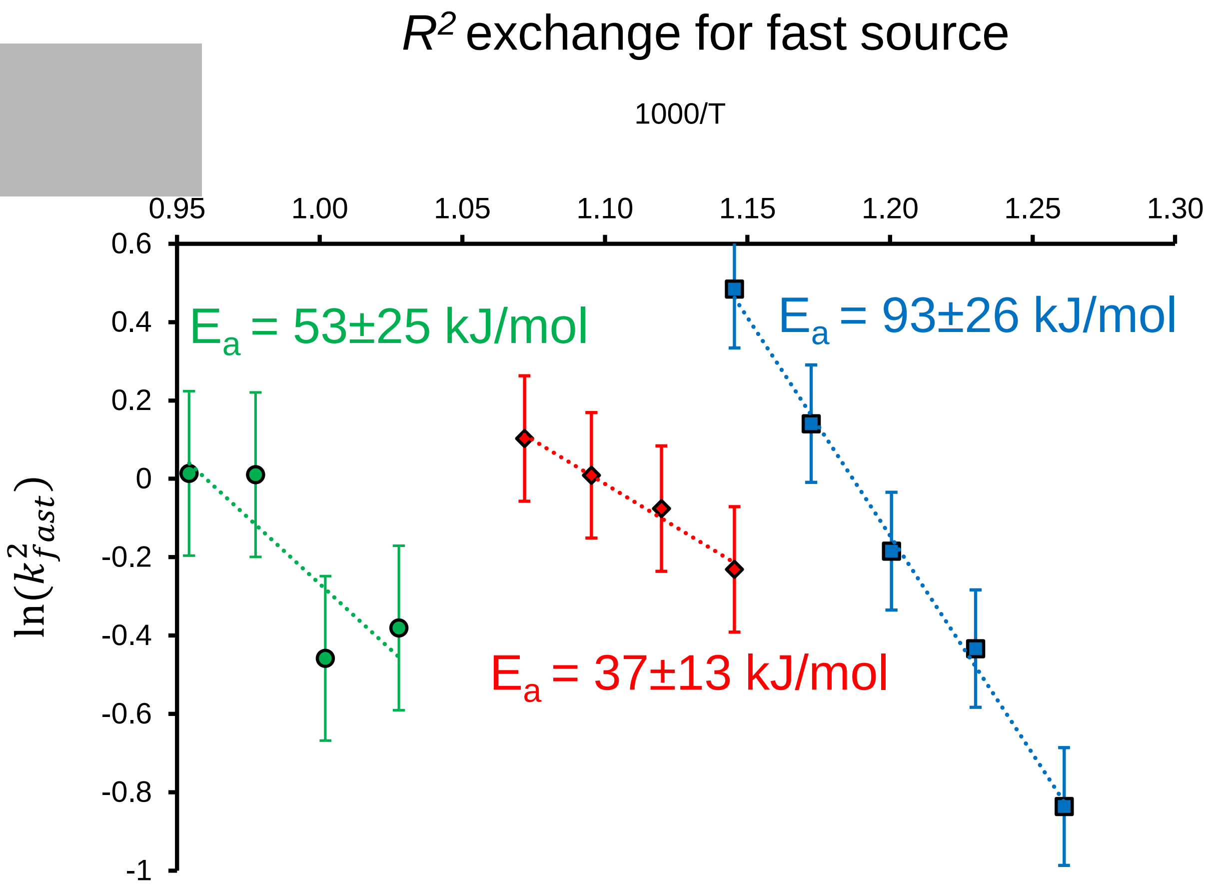
Artsiusheuski et al., JPCC, 2021, 125, 26512

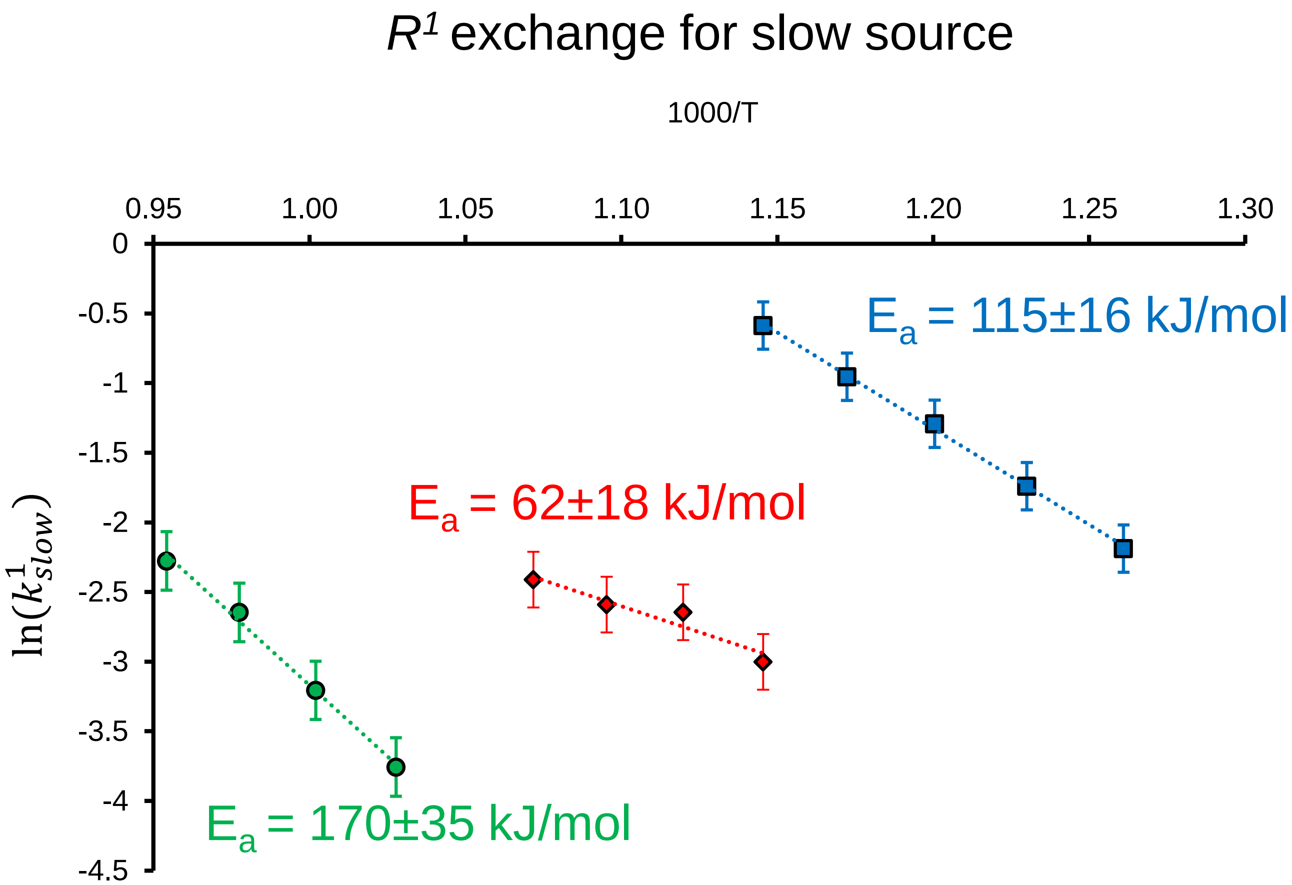
Effect of Si/Al ratio on the *C(O)*



The amount of exchangeable oxygen atoms in zeolite is independent of Si/Al ratio

Effect of Si/Al ratio on apparent E_a





● Cu(1.2)MOR(46) ◆ Cu(3.5)MOR(10) ■ Cu(4.3)MOR(6)

Variation of the Si/Al ratio leads to change in apparent E_a, possibly due to presence of different Cu species

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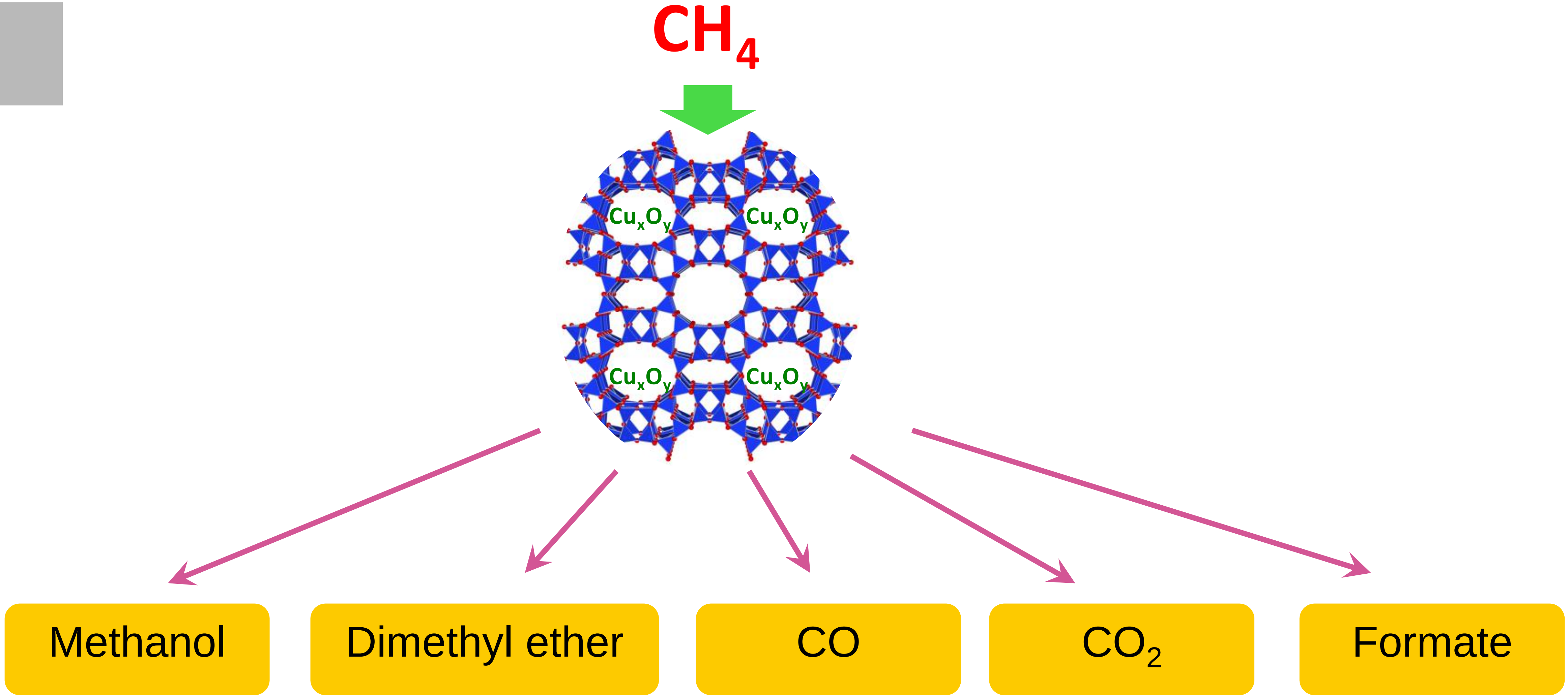
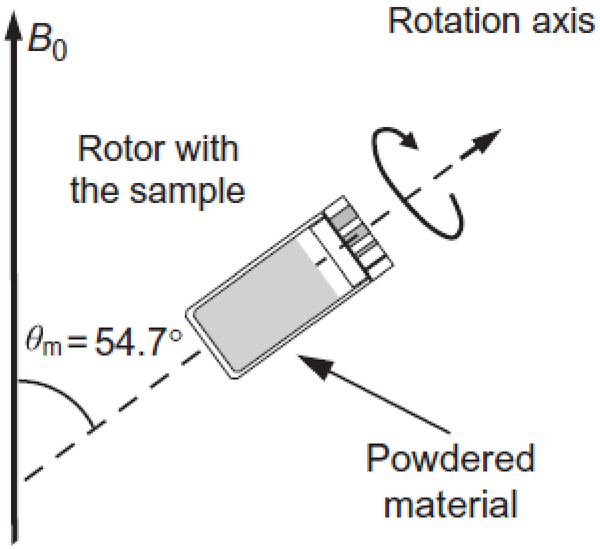
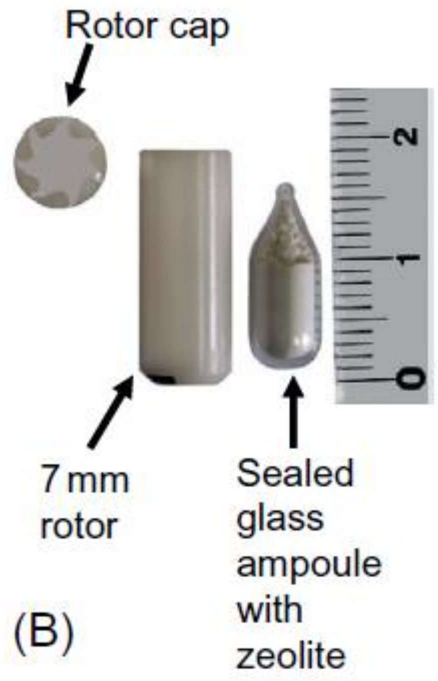
A zoo of products reported for the conversion of methane over copper-zeolites



Methods to follow the fate of methane: *in situ* MAS NMR and FTIR

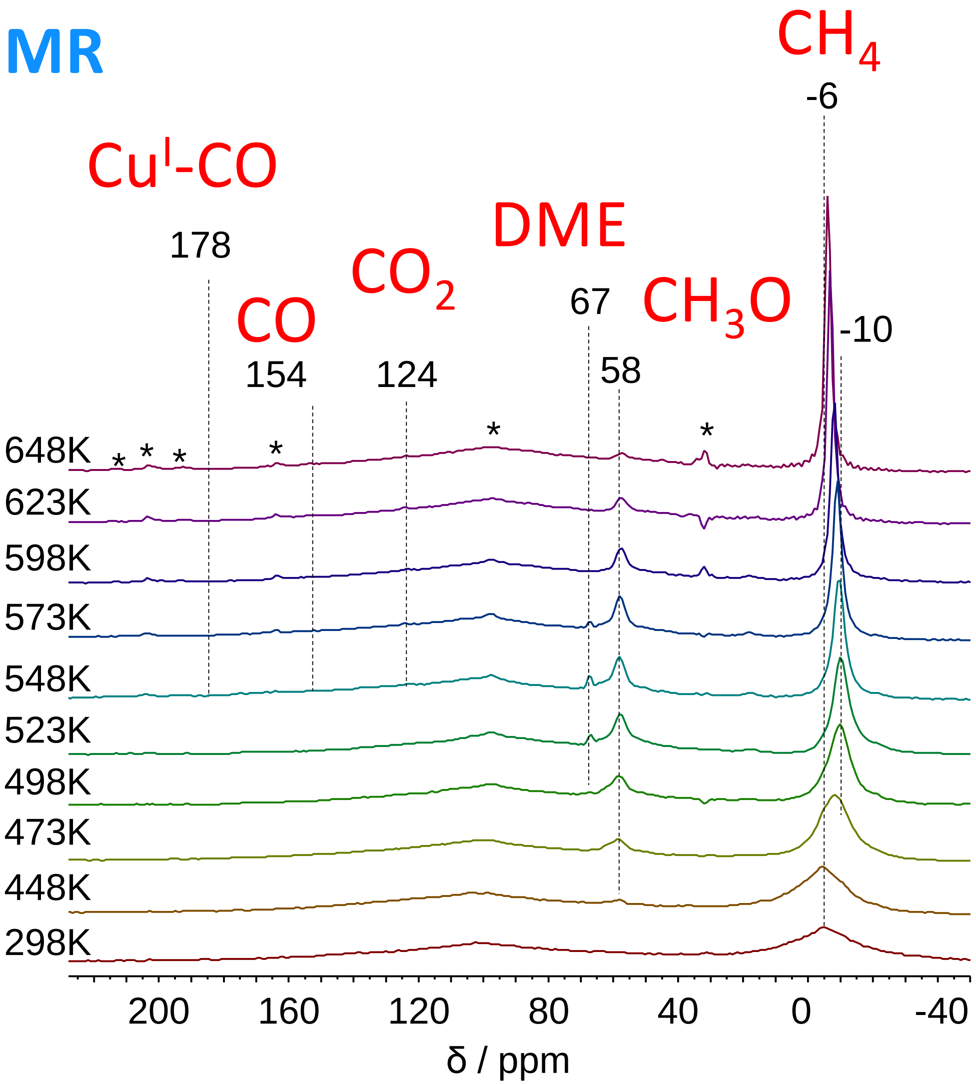




CuMOR, Si/Al = 6.5, activation: O_2, 673 K, 1 h vac 673 K, MAS 4 kHz, 1 mmol $^{13}CH_4$/g

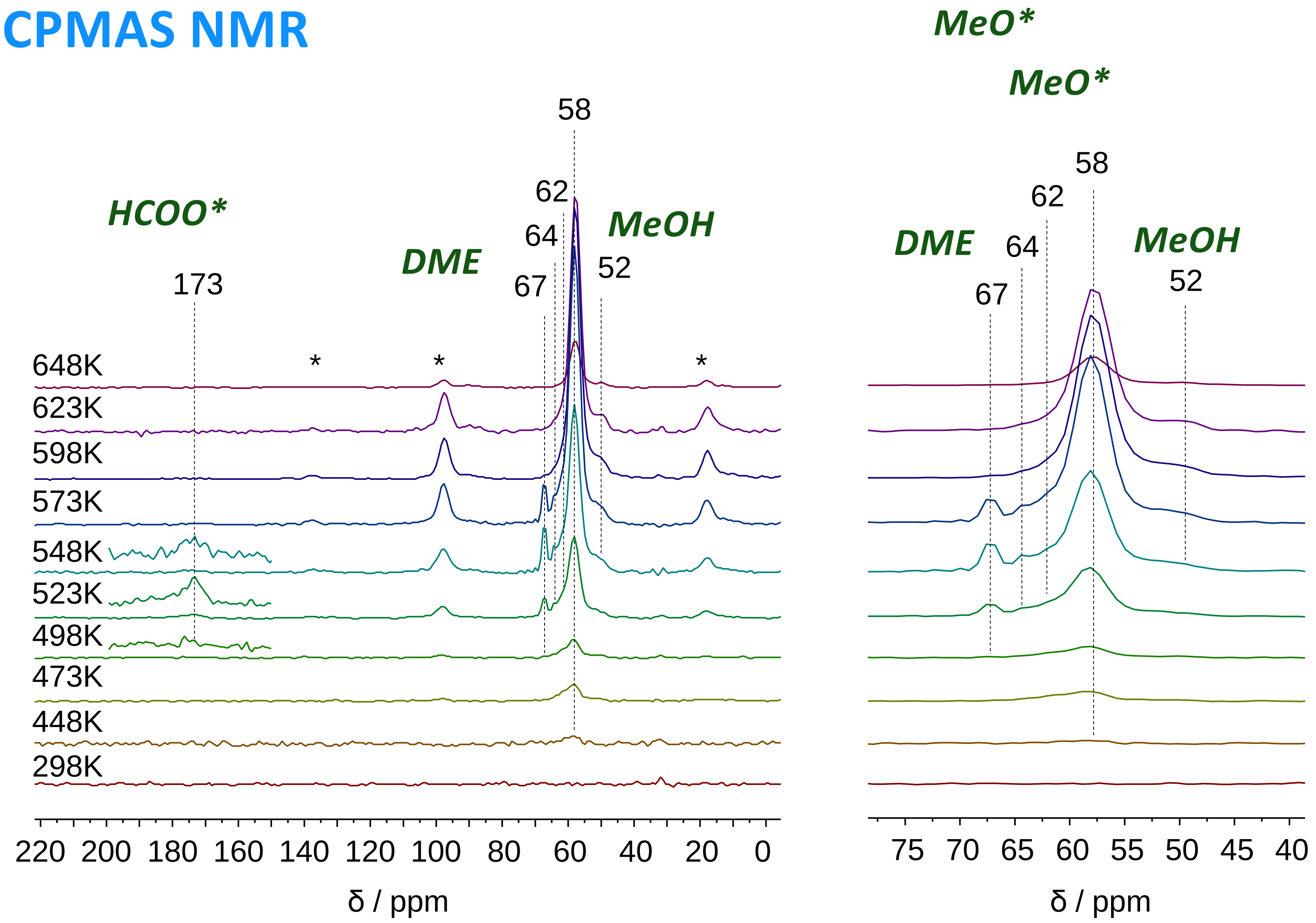
In situ NMR: CuMOR with Si/Al = 6

^{13}C HPDEC MAS NMR



In situ NMR: CuMOR with Si/Al = 6

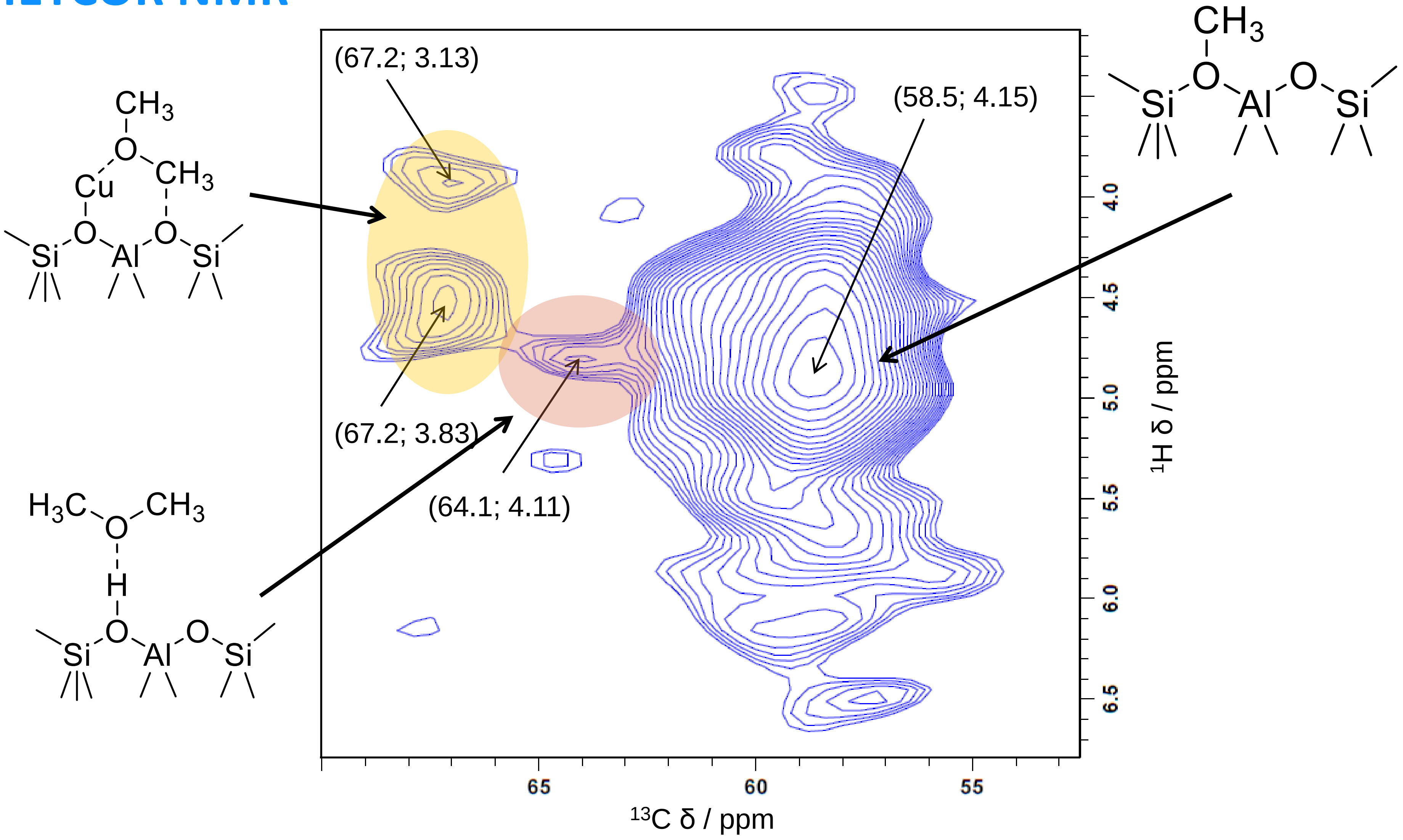
^{1}H-^{13}C CPMAS NMR



V. Sushkevich et al, ACIE, 2020, 132, 920-928

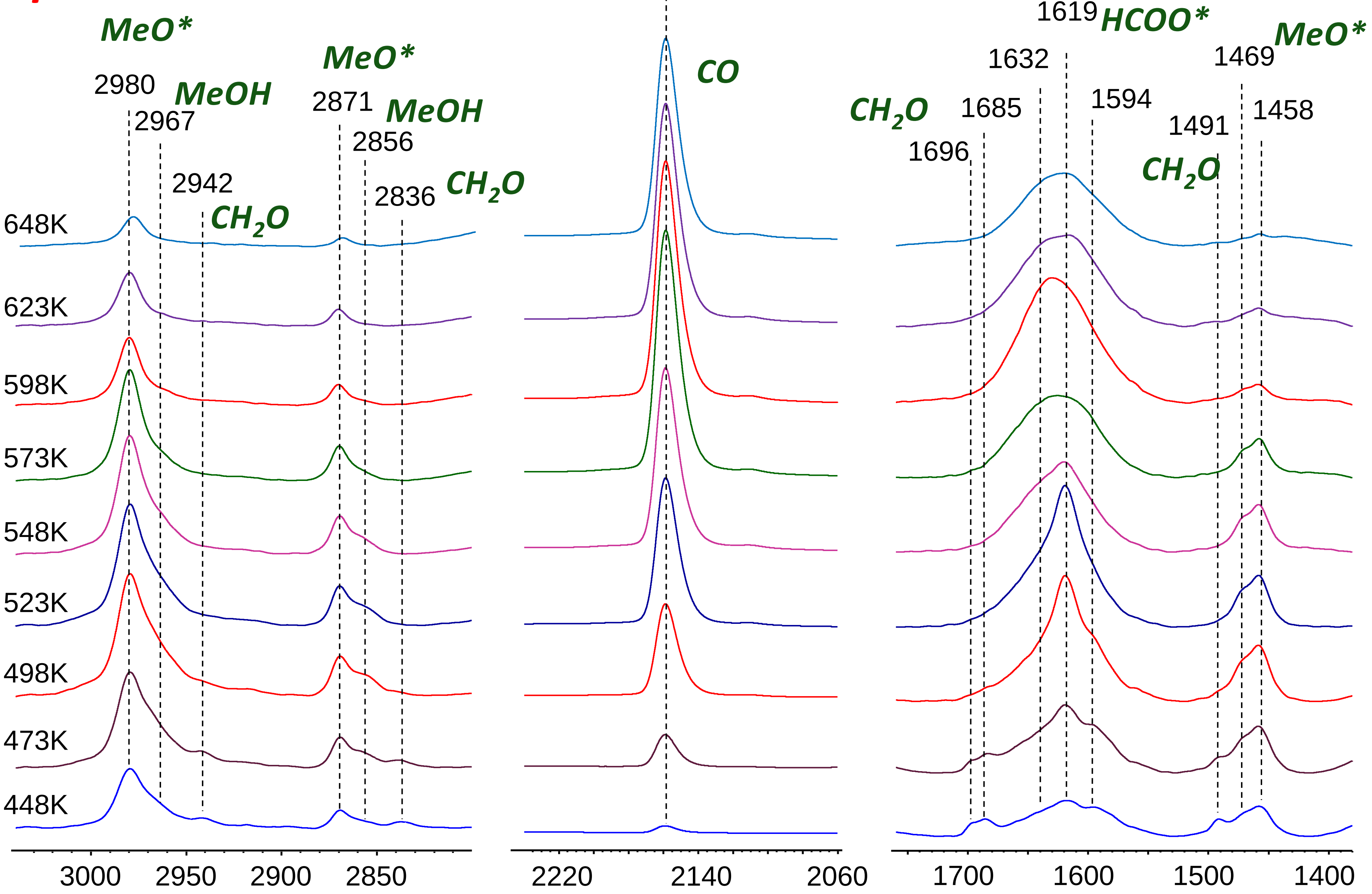
Identification of species observed by *in situ* NMR

^{1}H-^{13}C HETCOR NMR



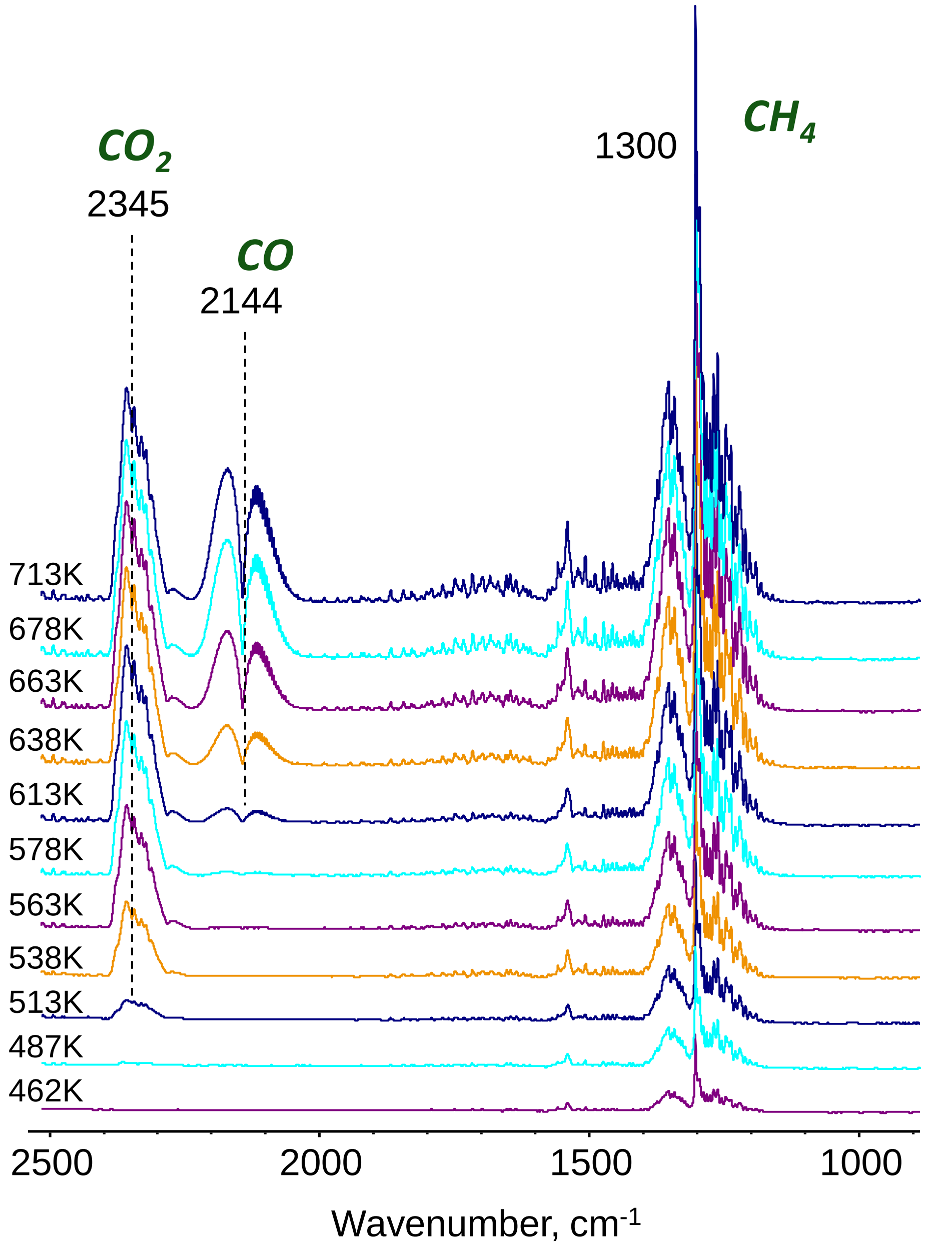
In situ FTIR: CuMOR with Si/Al = 6

Surface species

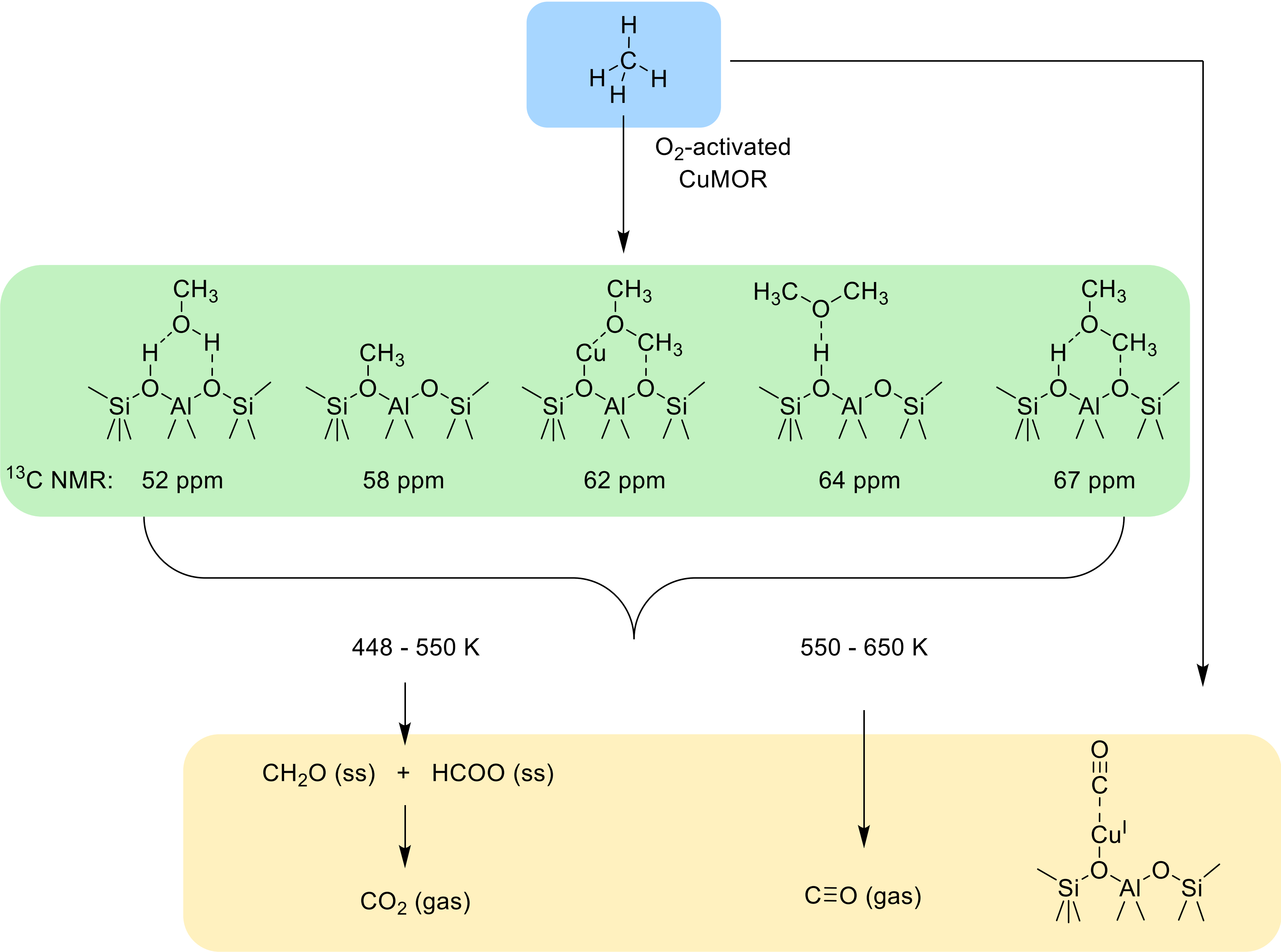


In situ FTIR: CuMOR with Si/Al = 6

Gas phase

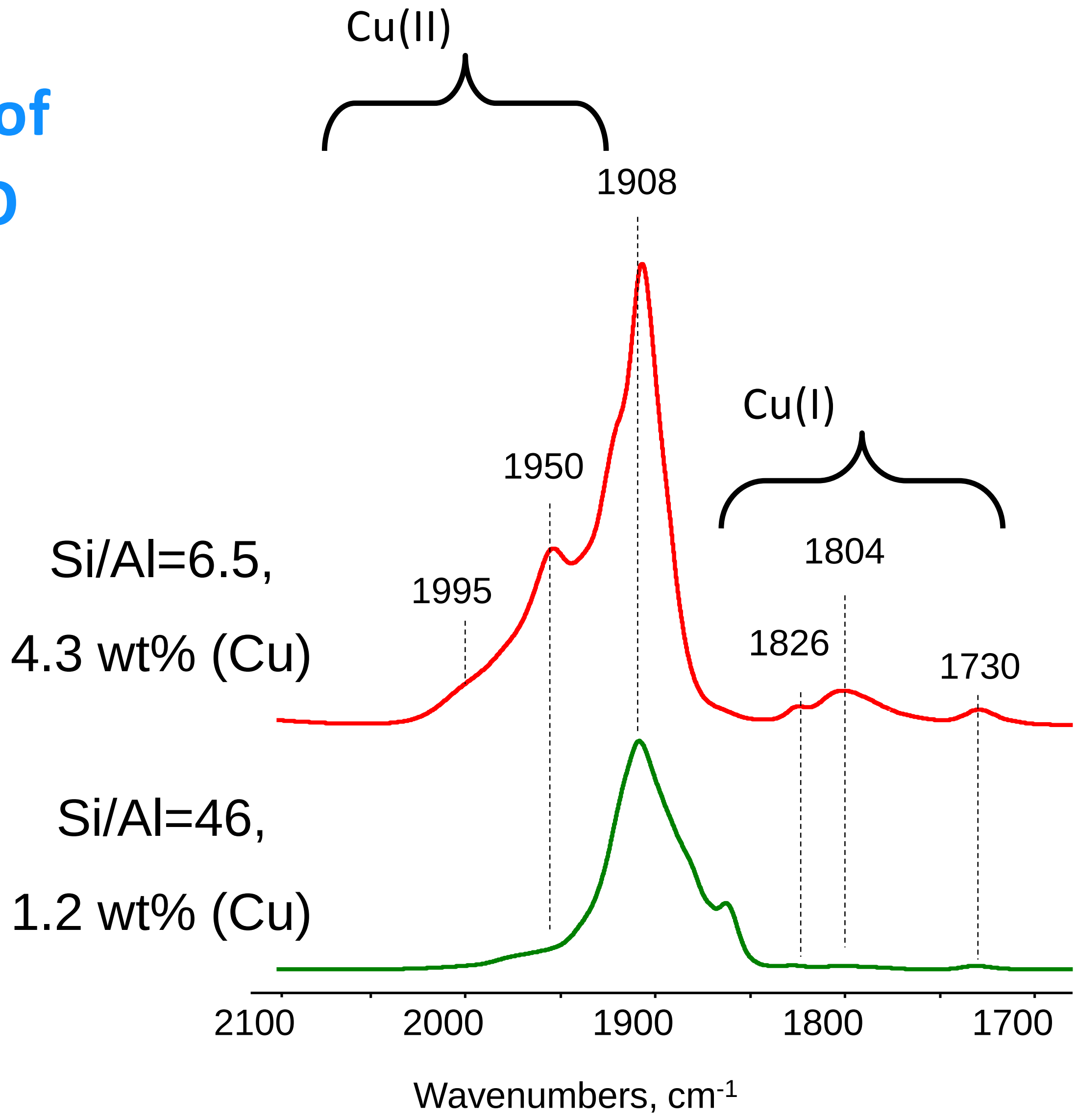


Reaction network as derived from MAS NMR and FTIR



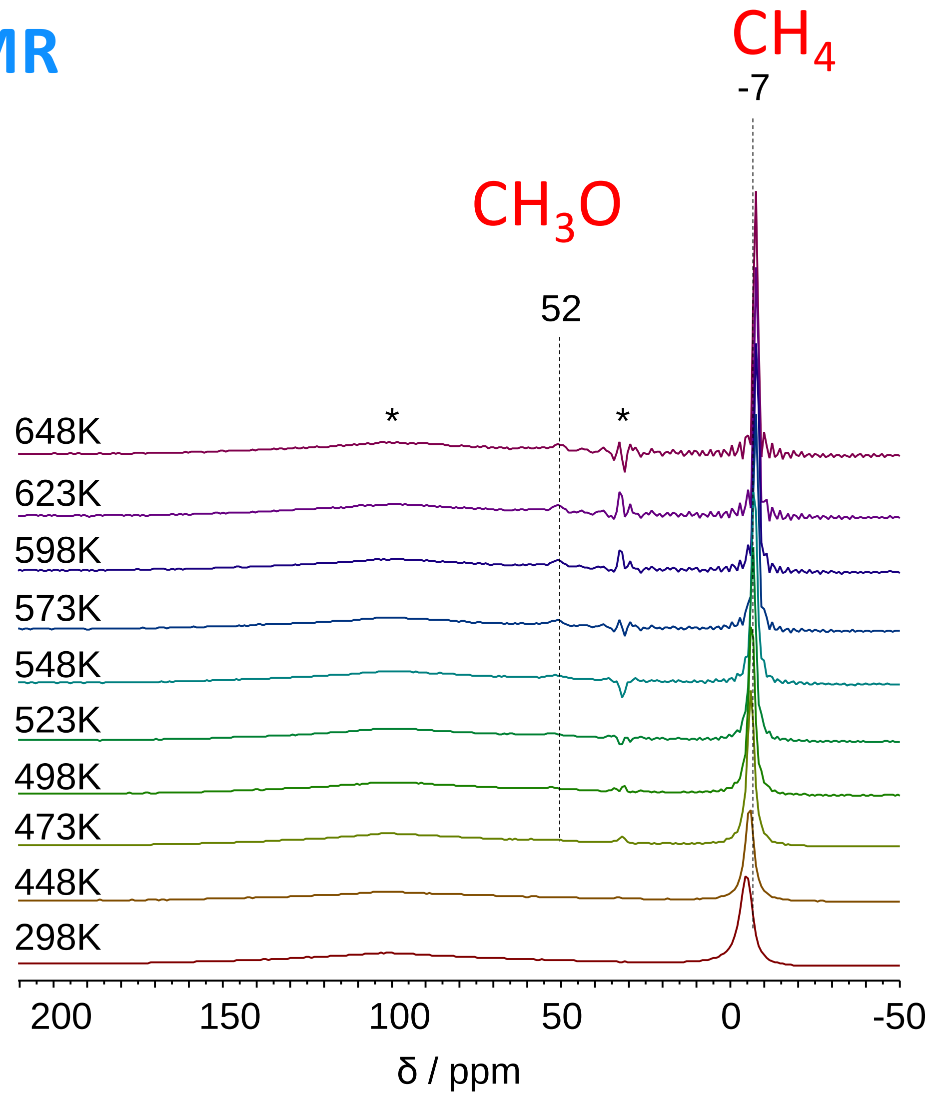
Reaction over the copper-exchanged mordenite with high Si/Al ratio

FTIR spectra of adsorbed NO



In situ NMR: CuMOR with Si/Al = 46

^{13}C HPDEC MAS NMR



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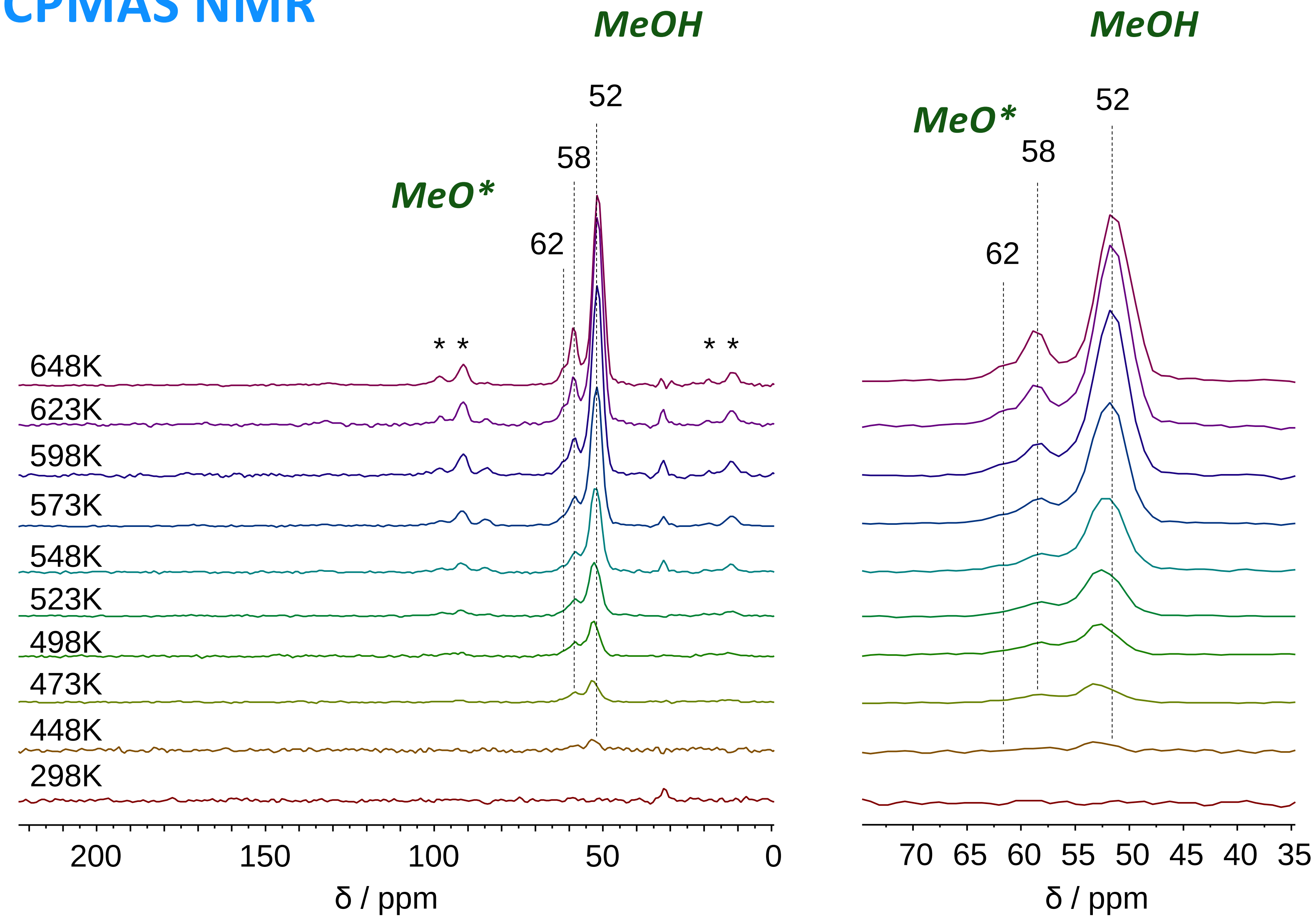
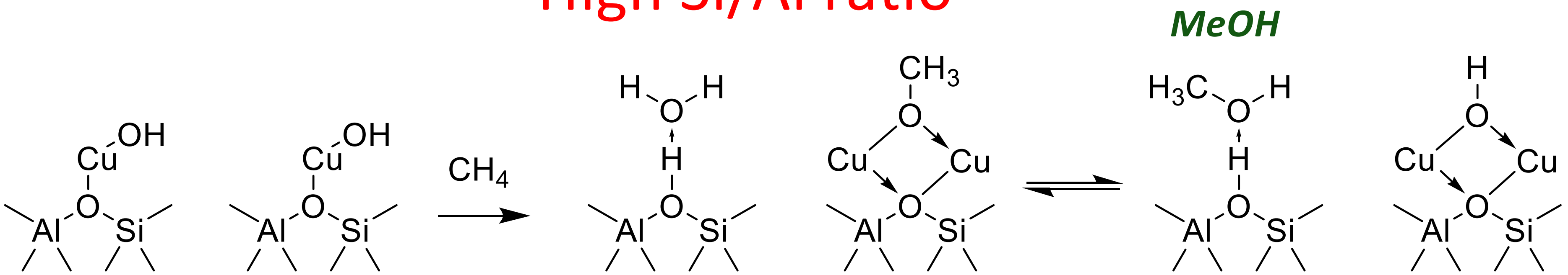
In situ NMR: CuMOR with Si/Al = 46

^{1}H-^{13}C CPMAS NMR

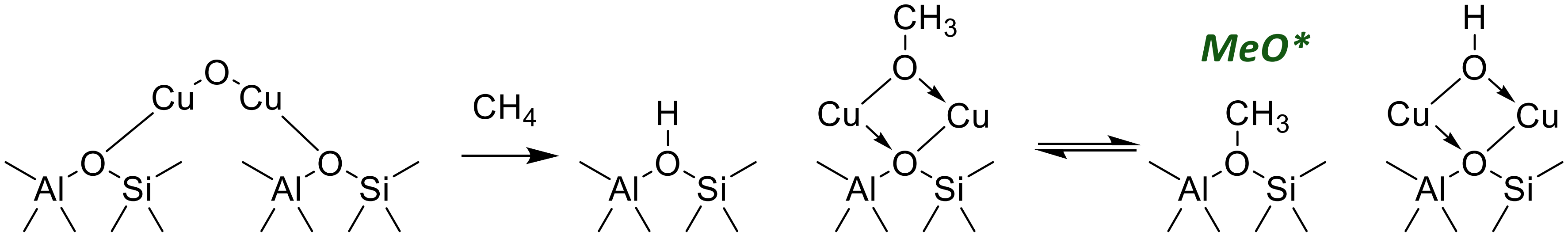


Methane to methanol: difference in active sites

High Si/Al ratio



Low Si/Al ratio



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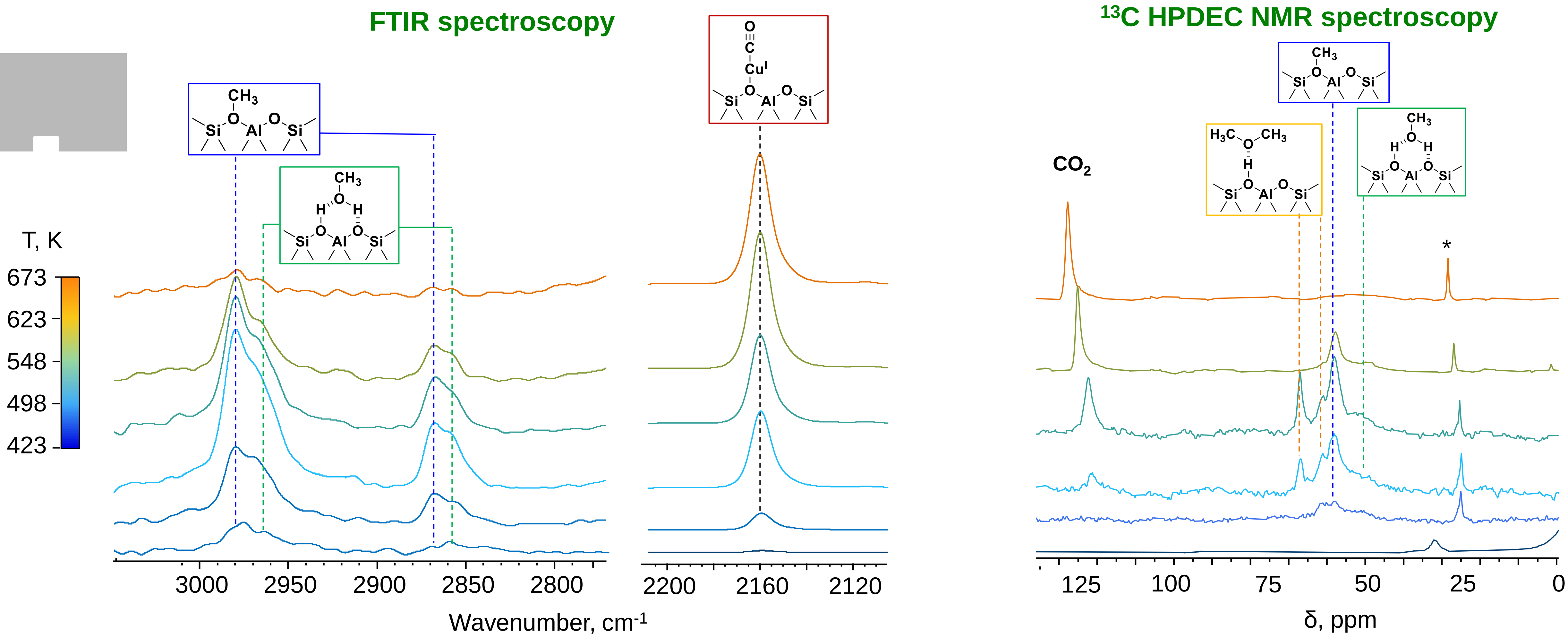
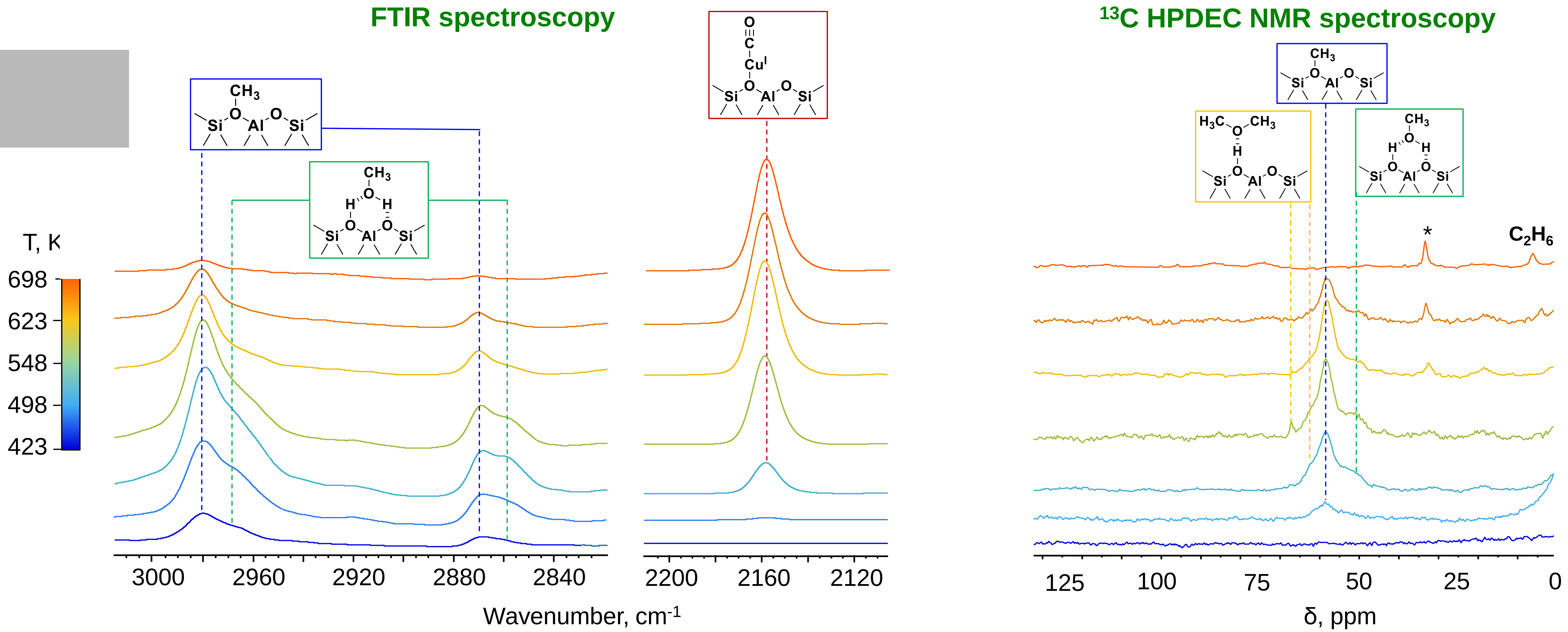
Reaction over Cu(4.0)MFI(12): FTIR and NMR



- MeO(BAS) and MeOH are formed < 550K
- Overoxidation to Cu(CO) and CO_2 > 550K

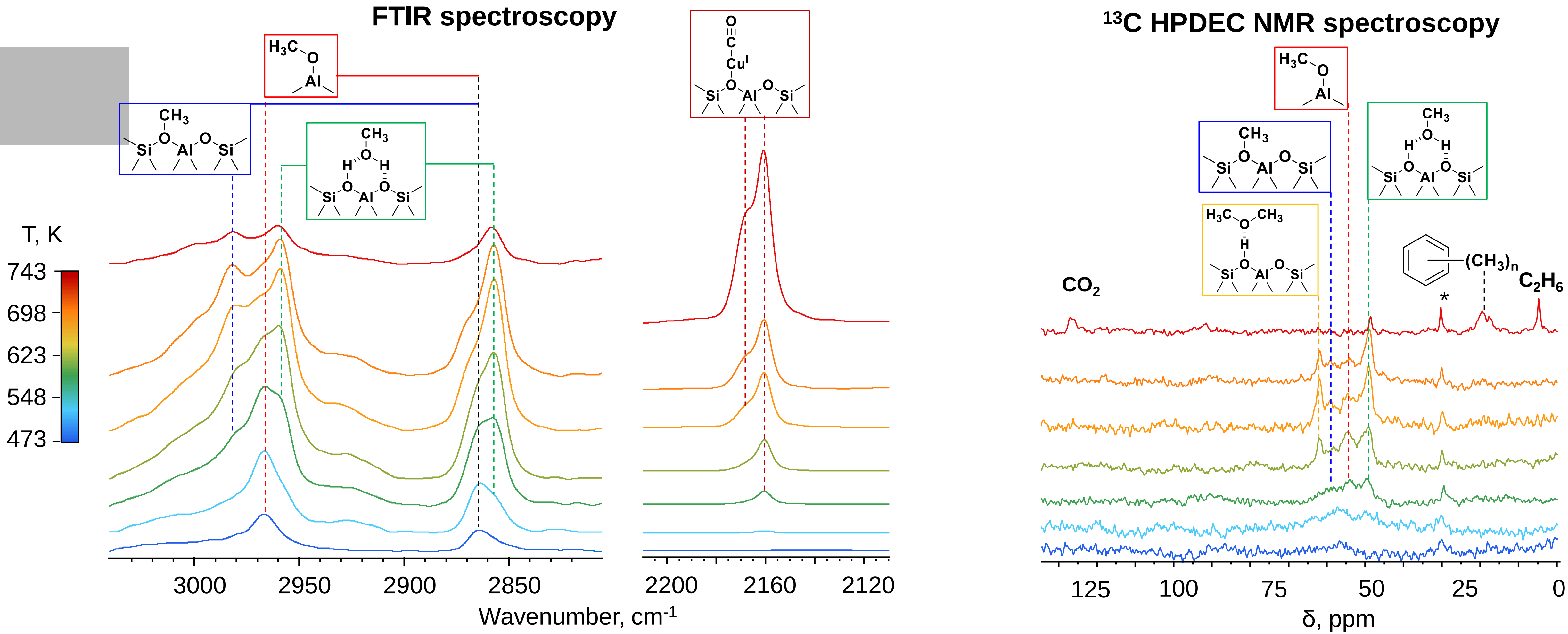
Artsiusheuski et al., ACS Catal., 2021, 11, 12543

Reaction over Cu(3.4)MOR(10): FTIR and NMR



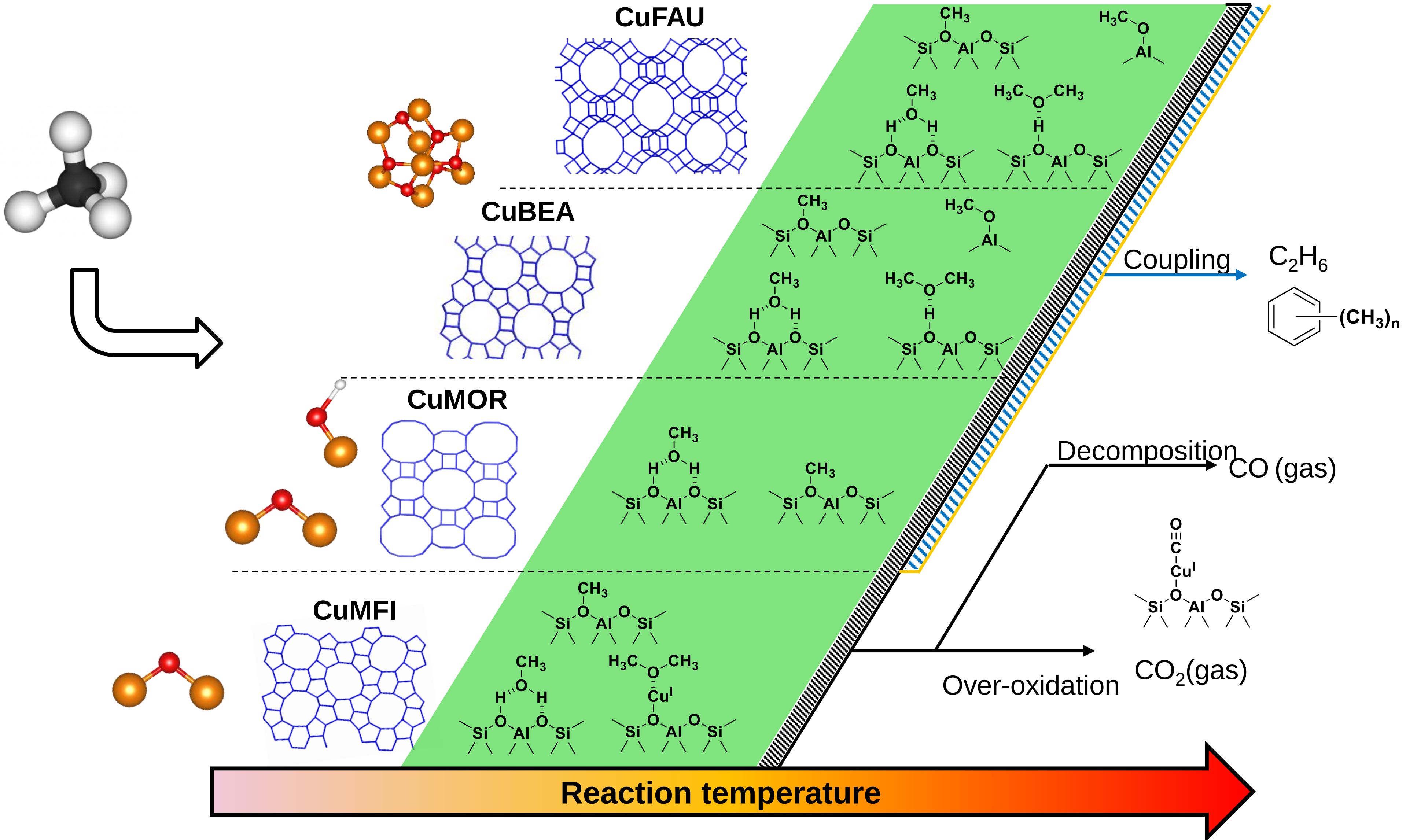
- Partial oxidation to methanol precursors < 550K
- Overoxidation to CO_2 not observed
- C_xH_y formed >600 K

Reaction over Cu(2.7)FAU(15): FTIR and NMR



- Partial oxidation products stable up to 700 K
- 2 different types of Cu(CO), CO_2 formed at 728 K
- C_xH_y formed >600 K

Summary of observed transformations over different CuZEOs



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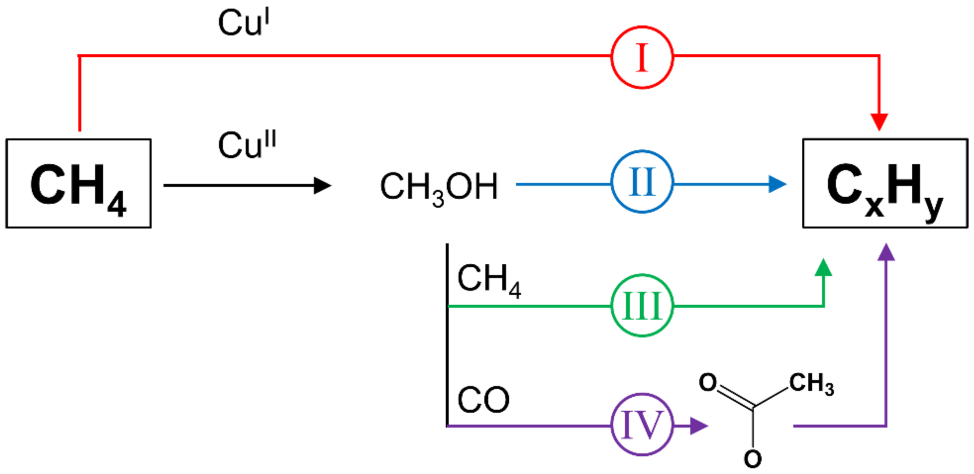
- Operando EPR and UV-vis

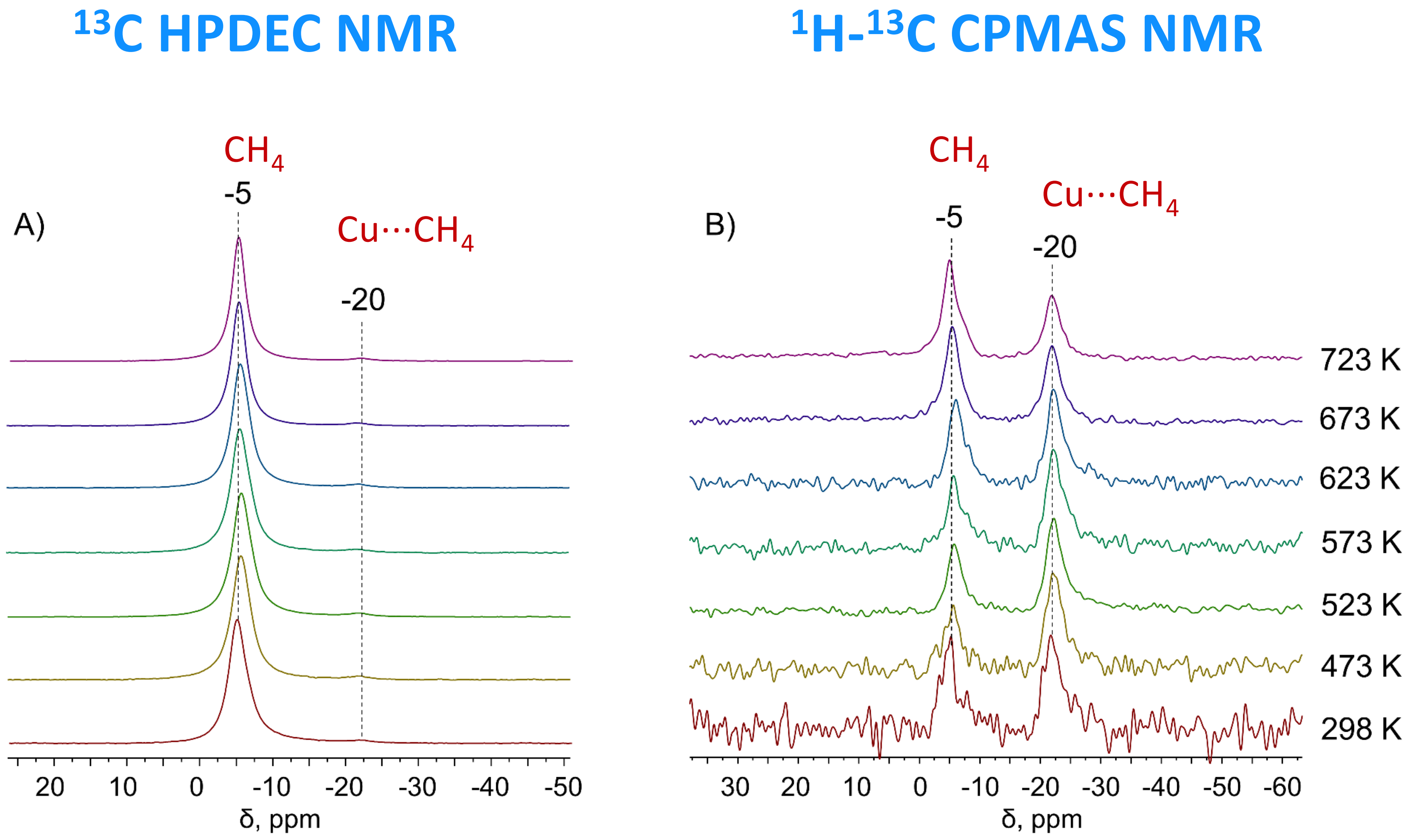
Experiment strategy – ^{13}C isotope tracing



Reaction route, *studied reaction mixture*

- (I) Direct coupling, *$Cu^{I}MOR$ + $^{13}CH_4$*
- (II) MTH-like process, *$Cu^{I}MOR$ + $^{13}CH_3OH$*
- (III) MTH involving CH_4, *$Cu^{I}MOR$ + $^{12}CH_3OH$ + $^{13}CH_4$*
- (IV) Koch carbonylation, *$Cu^{I}MOR$ + $^{12}CH_3OH$ + ^{13}CO*

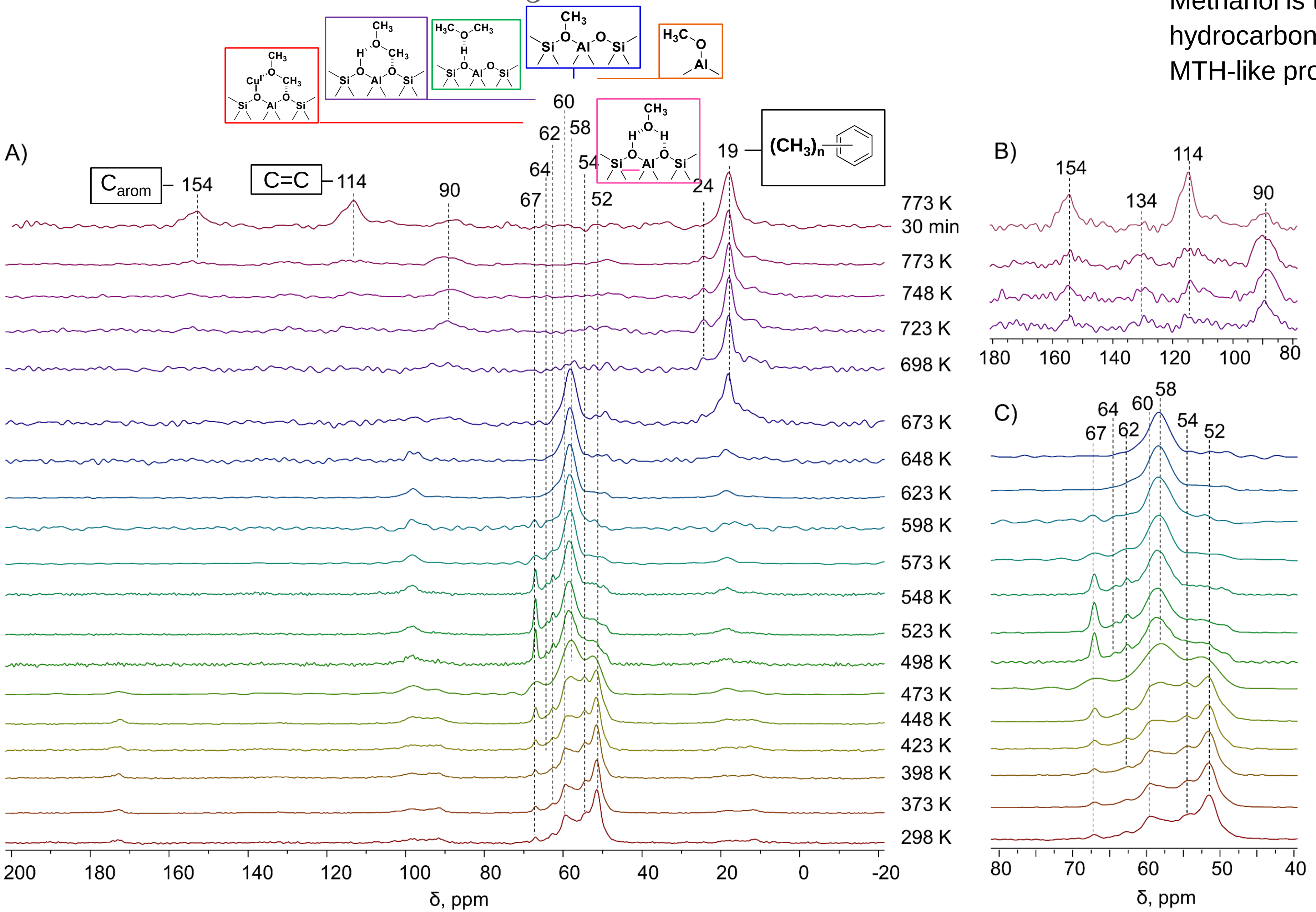
Reaction with $^{13}CH_4$



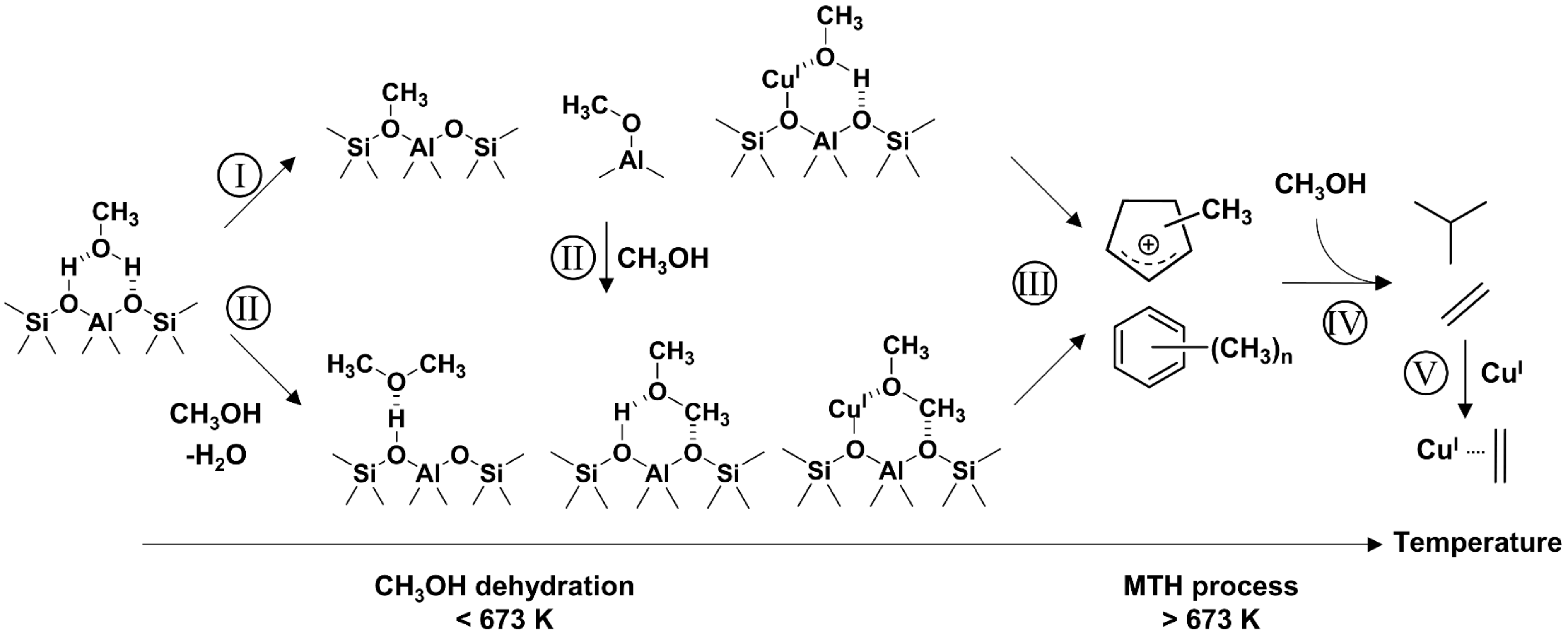
No direct coupling

Reaction of $^{13}CH_3OH$ over Cu^IMOR

Methanol is transformed to hydrocarbons, apparently via MTH-like process, over Cu^IMOR

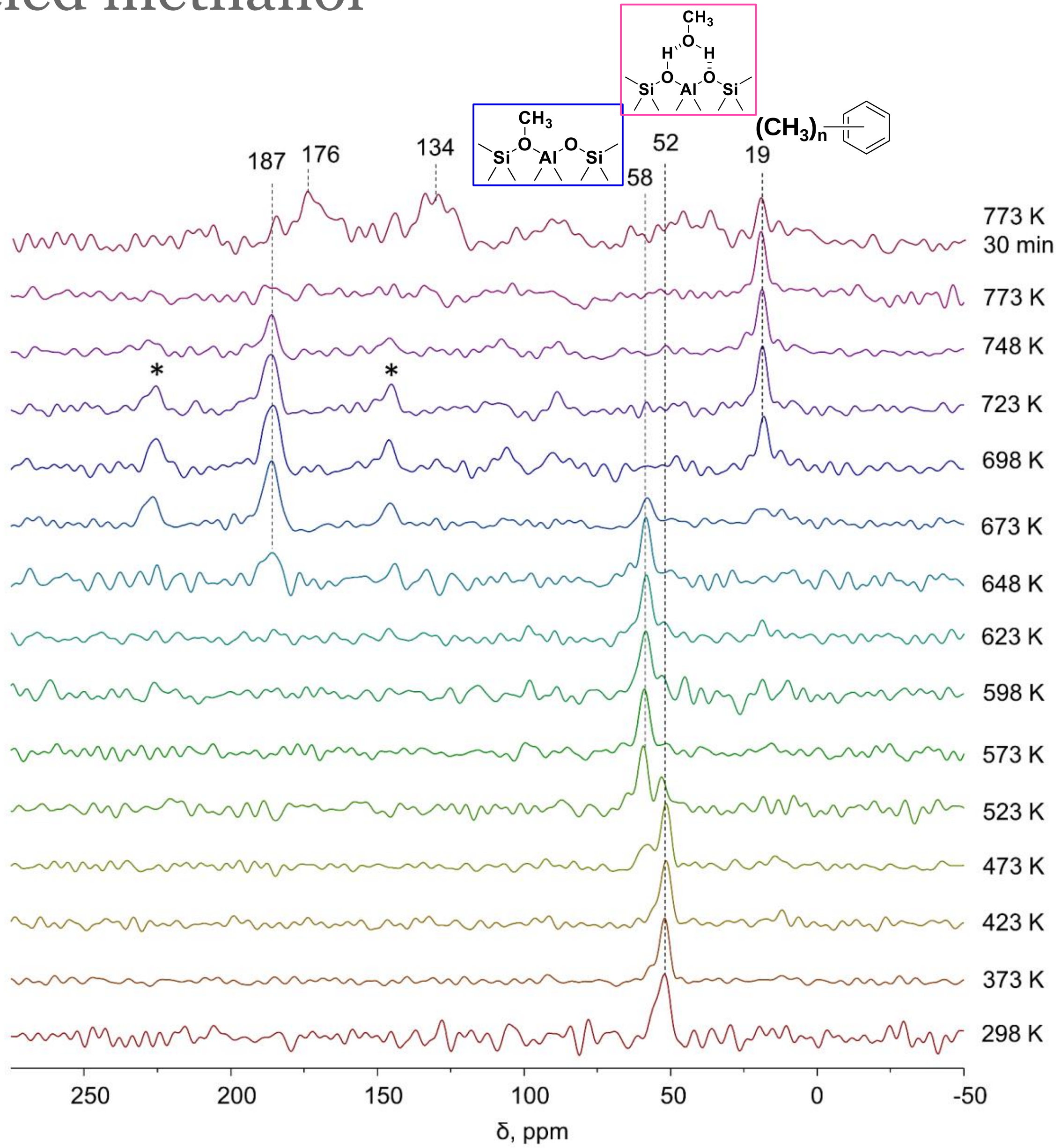


Observed reaction pathways for $^{13}CH_3OH$

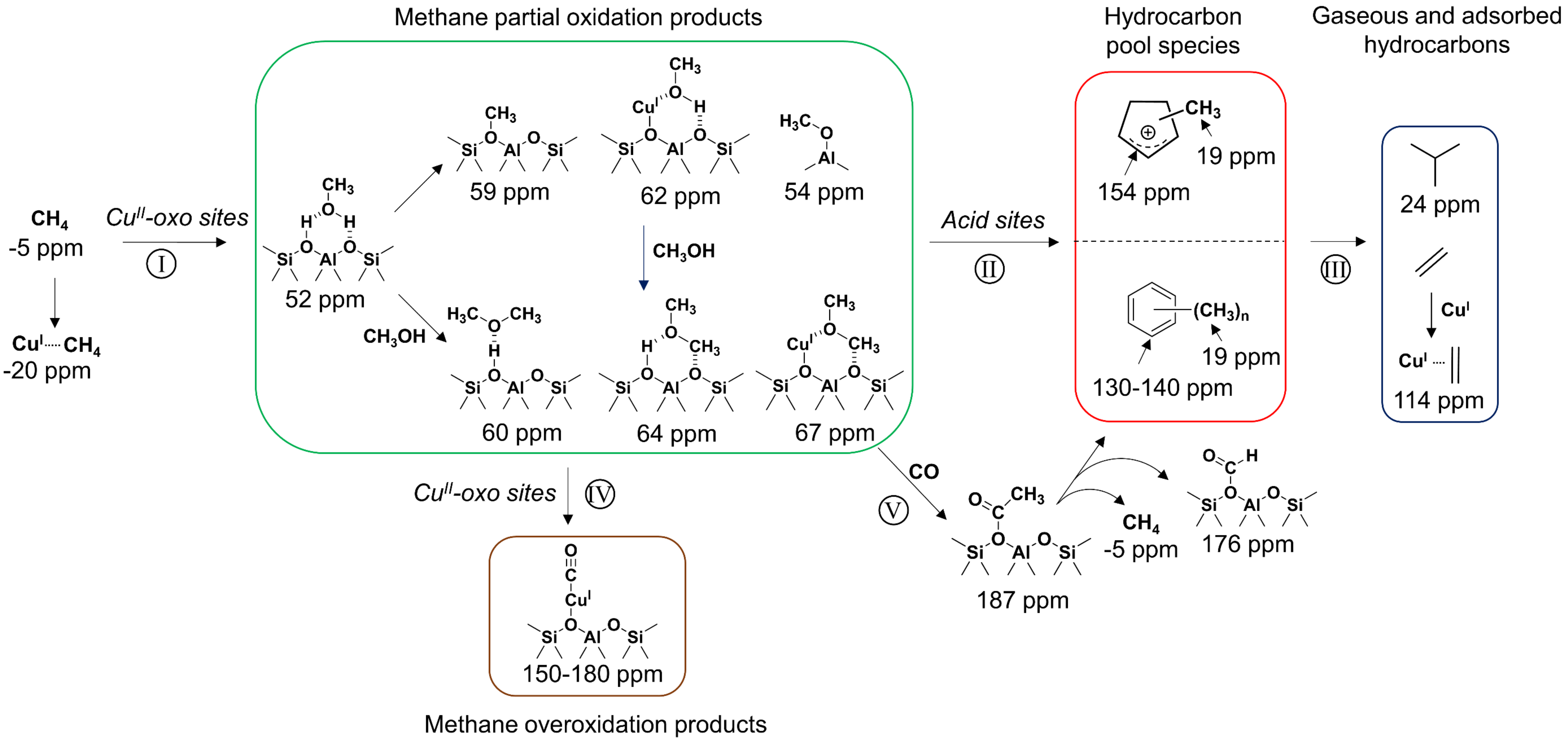


Artsiusheuski et al., JACS, 2022, submitted

Impact of Koch carbonylation: reaction of ^{13}CO with non-labeled methanol



Reaction network



PAUL SCHERRER INSTITUT PSI

In situ and operando study of direct methane conversion to methanol

$CH_4 \rightarrow CH_3OH$

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Active sites

- XAS study of Cu species
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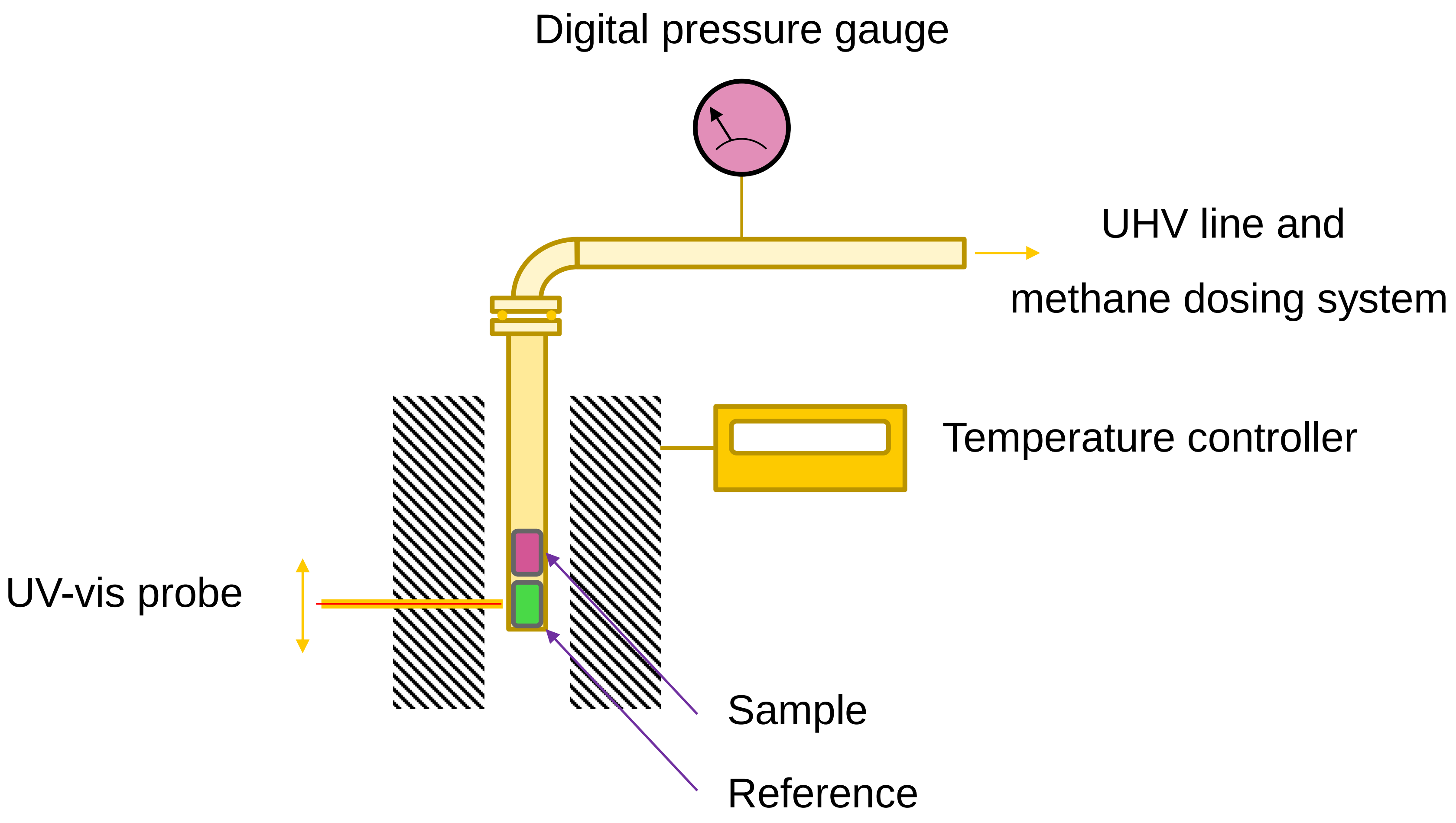
Operando

Site-specific kinetics

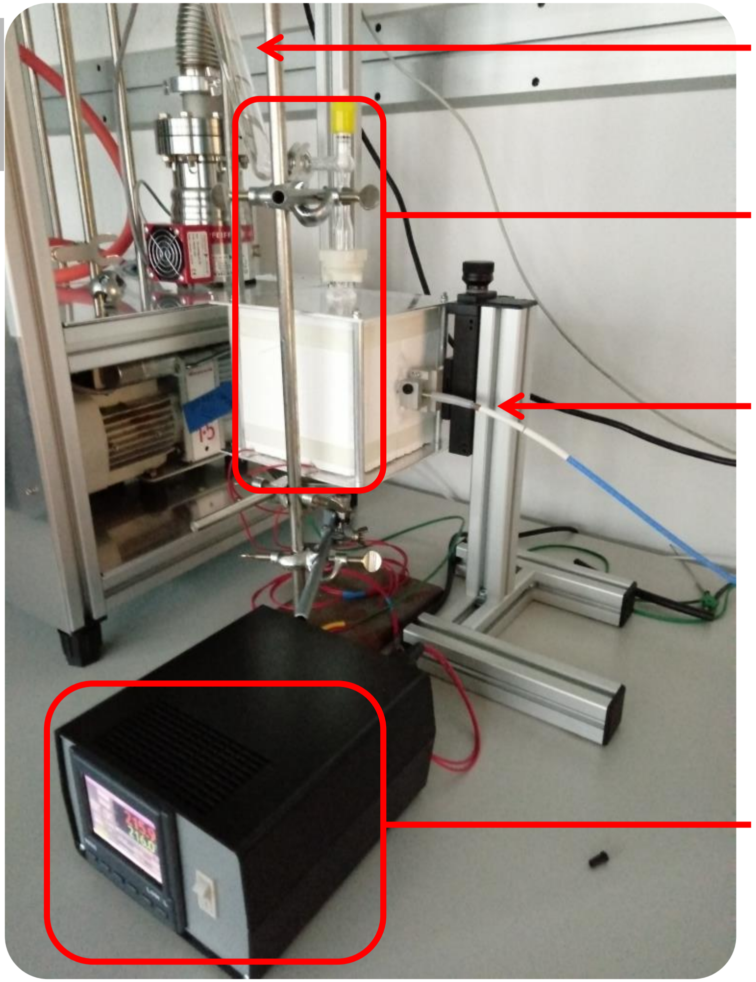
- **Operando UV-vis powered by in situ EPR**
- Operando EPR and UV-vis

Establishing intrinsic kinetic parameters for different copper species



$$CH_{4(gas)} + [Cu\text{-}O\text{-}Cu]^{2+}_{(solid)} = [CH_3\text{-}(OCH_3)\text{-}Cu]^{+}_{(solid)} + H^{+}_{(solid)}$$

In Situ UV-Vis (DRS) Equipment



Connection line

UV-Vis quartz cell/

Insulating block

Reflection probe/

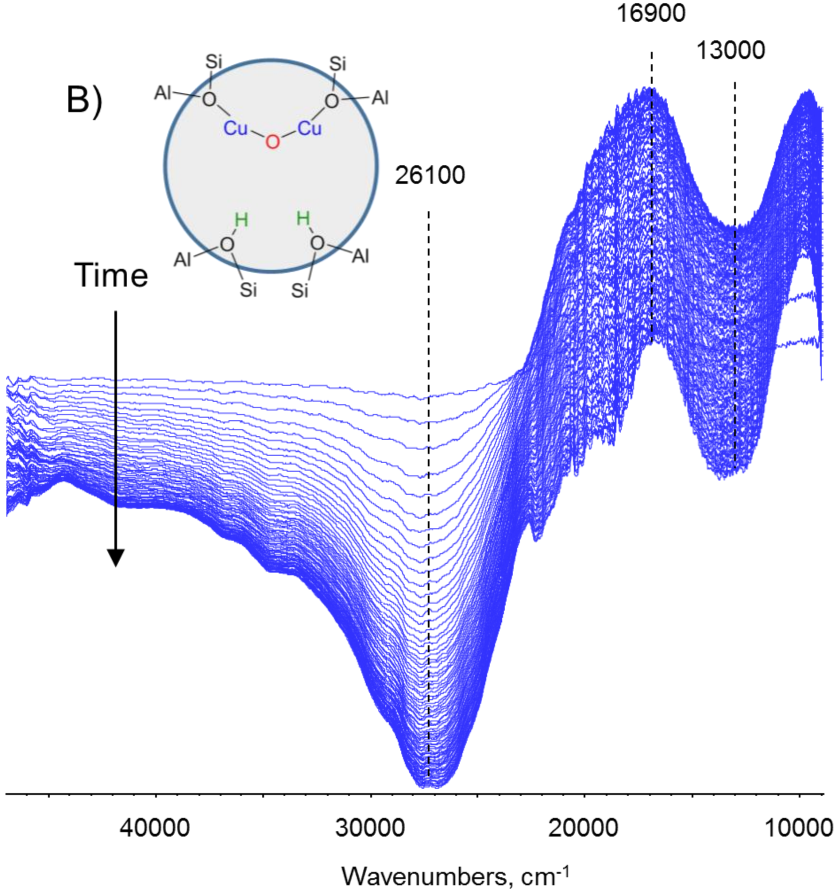
Adjustable clamp

Temperature controller

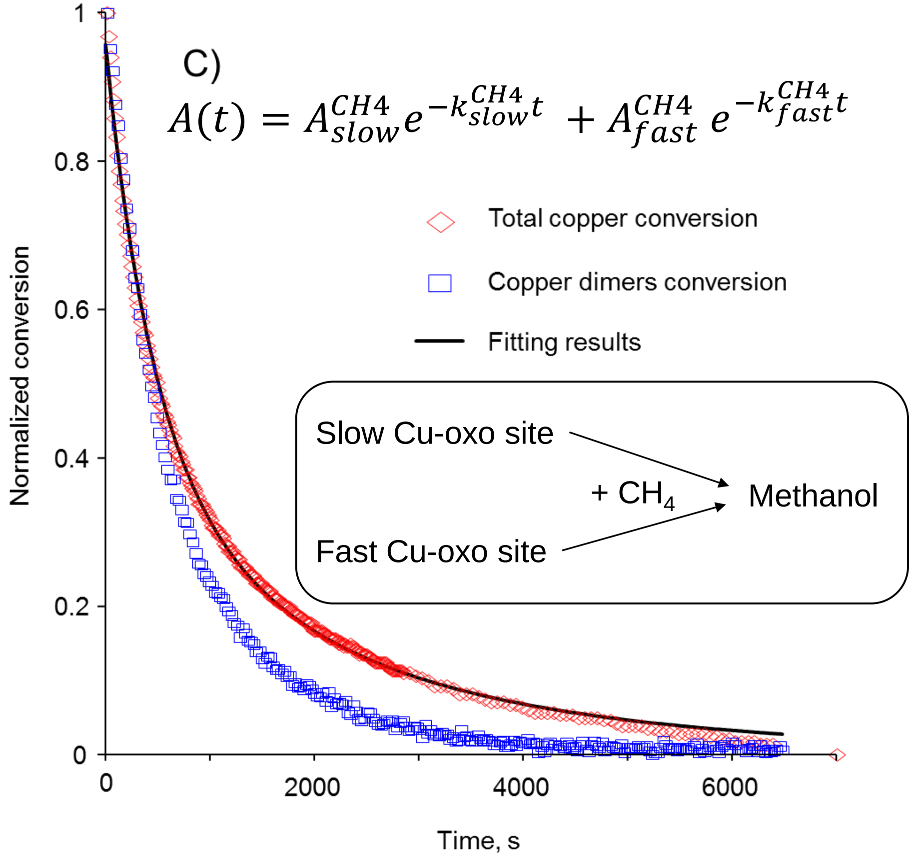
- Wavelength range: 200 – 1100 nm
- Resolution: 0.035 nm (FWHM)
- Integration time: down to 17 ms

Establishing intrinsic kinetic parameters for different copper species

Subtracted UV-vis



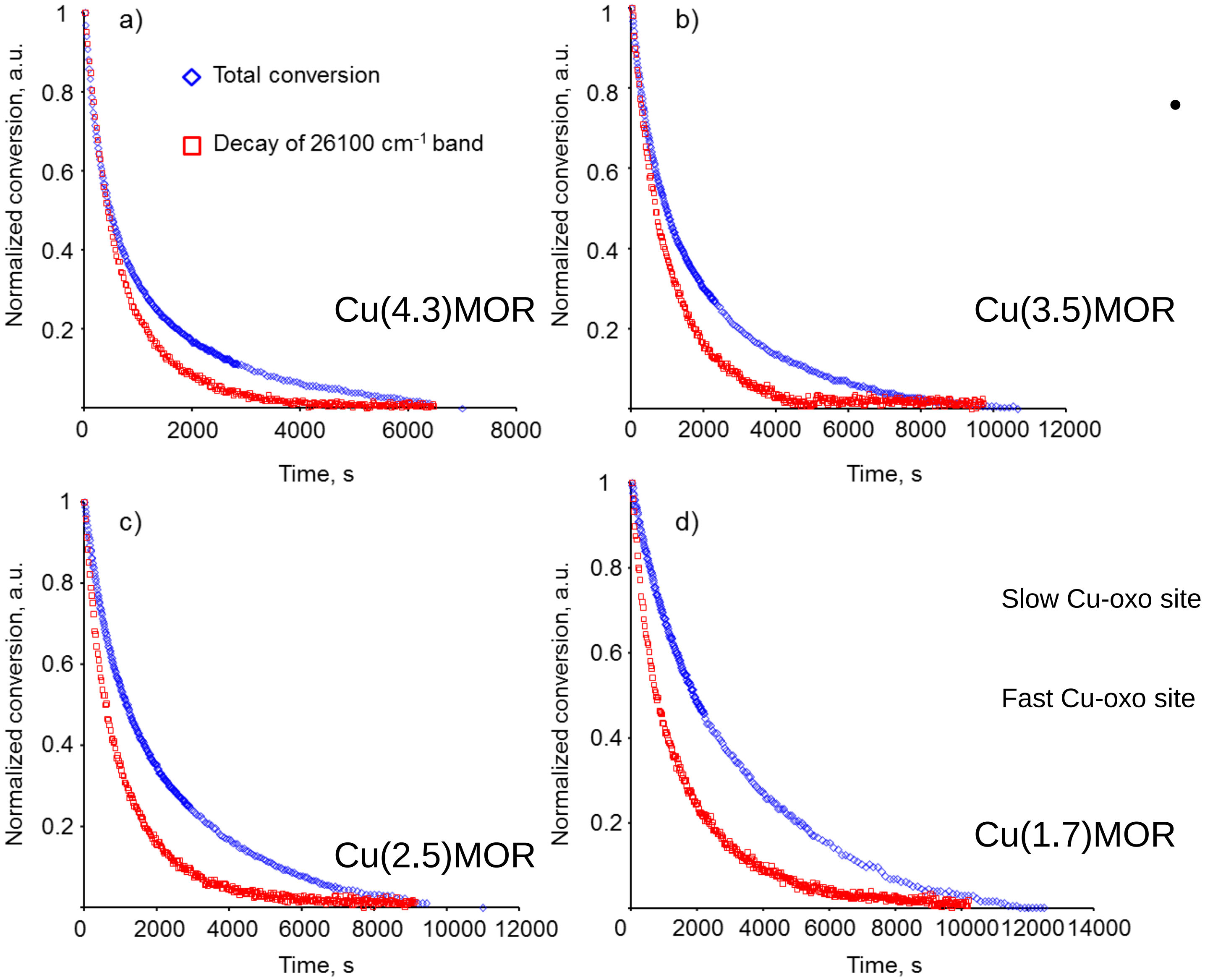
Normalized kinetic response



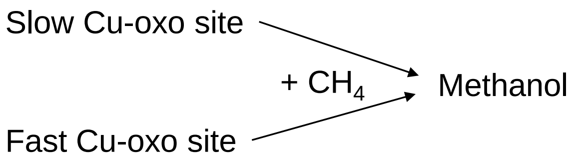
- Time-resolved UV-vis shows the consumption of dimeric species
- Total conversion can not be described by single conversion of dimers, other species contribute as well

Sushkevich et al., Angew. Chem. Int. Ed., 2021, DOI: 10.1002/anie.202101628

Establishing intrinsic kinetic parameters for different copper species



- In samples with less copper and less dimers the difference in kinetic behavior of dimers and total activity is even more pronounced



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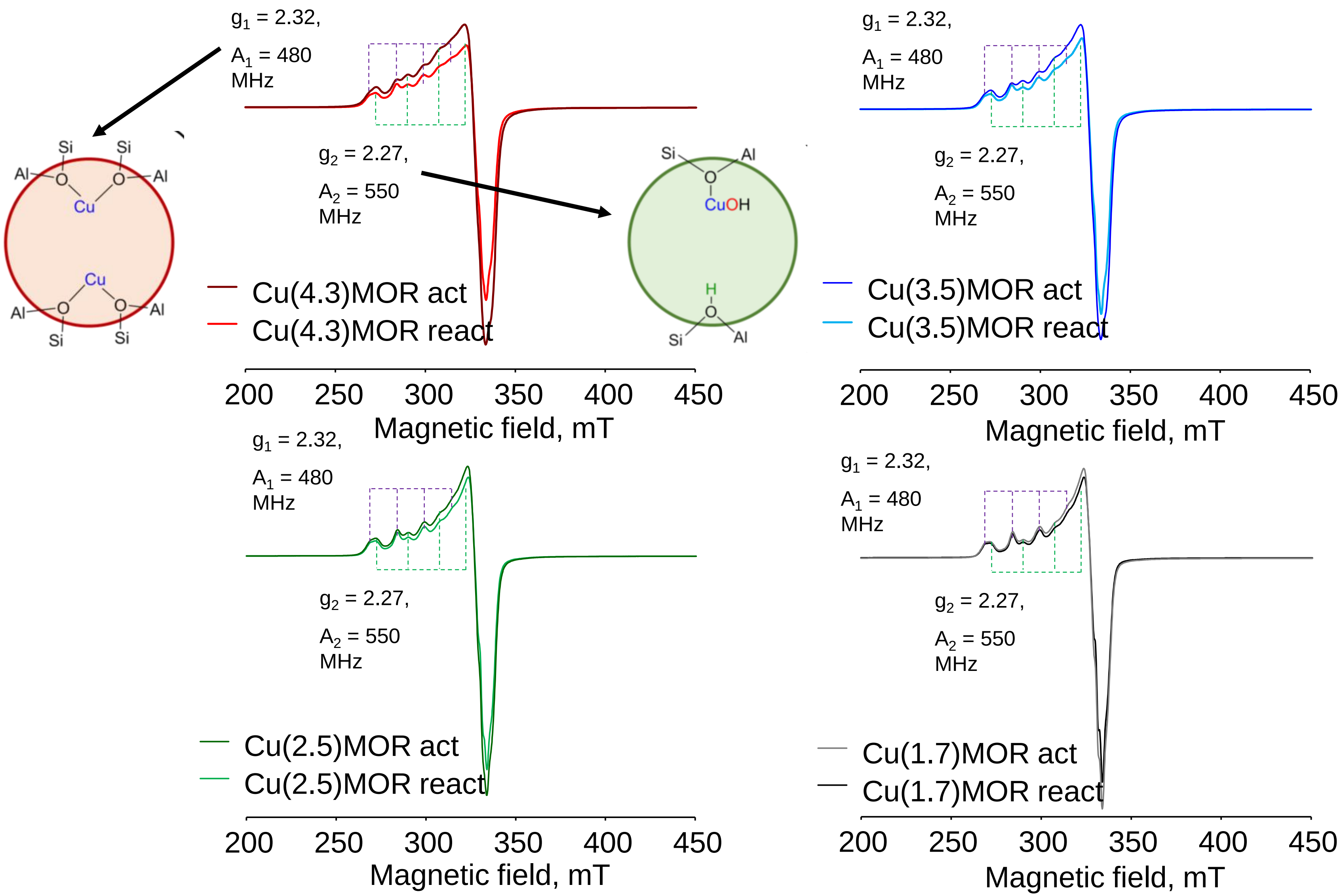
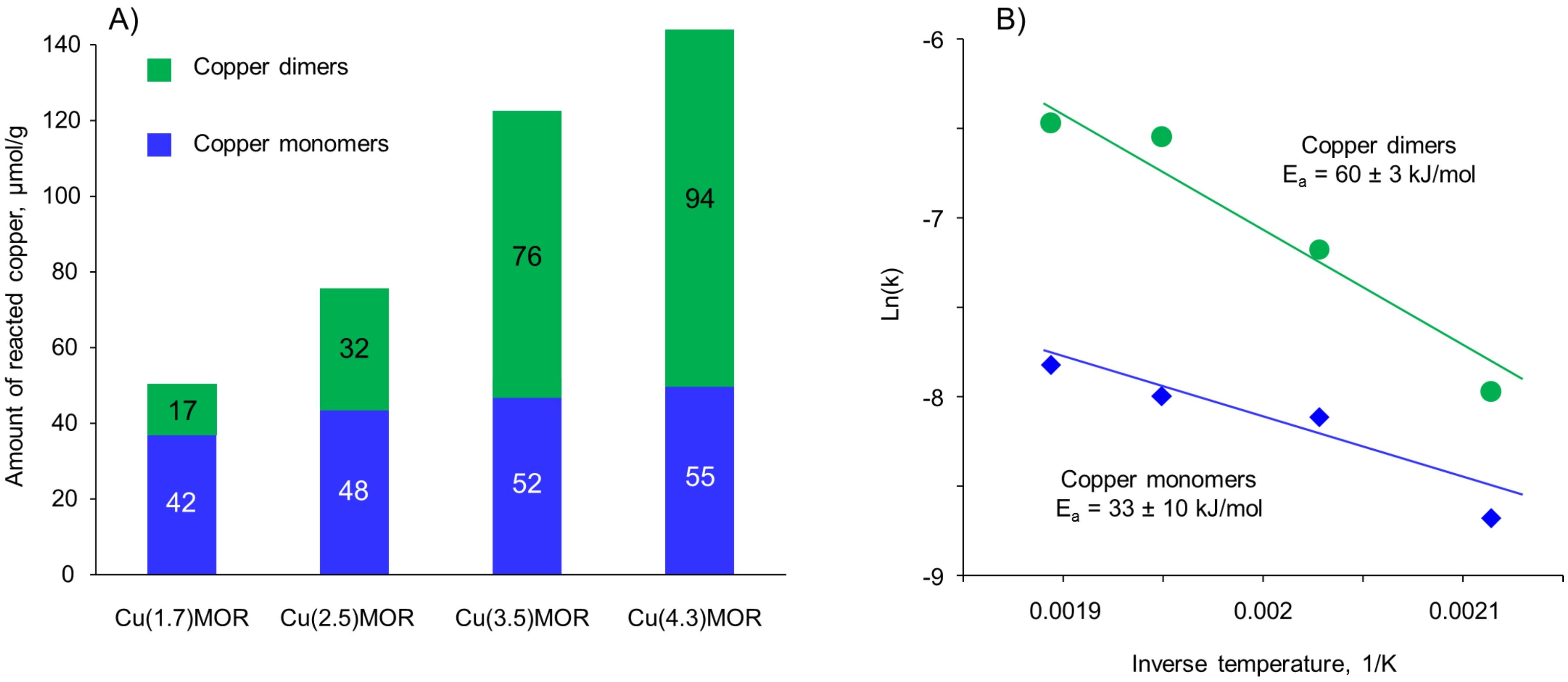
Establishing intrinsic kinetic parameters for different copper species

CW EPR before and after reaction



Establishing intrinsic kinetic parameters for different copper species



- Concentration of monomers in preserved and the excess of copper goes to the formation of dimers, according to the fitting of kinetic data
- Monomers are has lower kinetic constants, but the activation energy is lower.
- For dimers, a good fit to the previous literature data and DFT is observed

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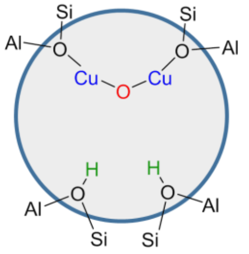
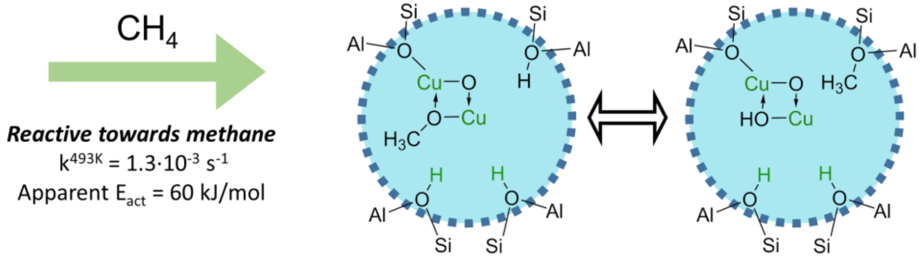
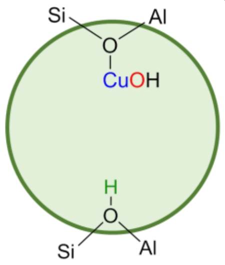
Establishing intrinsic kinetic parameters for different copper species

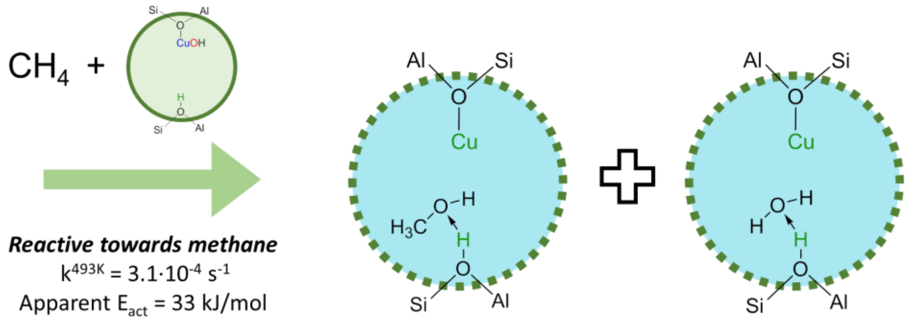
- IR bands of adsorbed NO with high frequency (> 1940 cm^{-1})
- Cu K-edge EXAFS scattering path with d(Cu-Cu) = 2.86Å, fraction > 20%
- UV-vis band at 26100 cm^{-1}
- Facilitated exchange with gas phase $^{18}O_2$
- High reducibility in TPR-CH_4



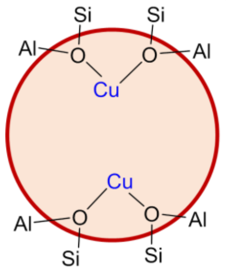


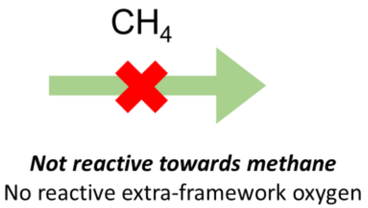
- IR bands of adsorbed NO with low frequency (~ 1910 cm^{-1})
- UV-vis band at 13000 cm^{-1}
- EPR signals with g = 2.27 and A = 550 MHz
- Hindered exchange with gas phase $^{18}O_2$





- IR bands of adsorbed NO with low frequency (~ 1910 cm^{-1})
- UV-vis bands at 16600 cm^{-1}
- EPR signals with g = 2.32 and A = 480 MHz
- EPR half-field transition signal, indicating Cu-Cu separation within the range of 5.5-7.0Å





Sushkevich et al., Angew. Chem. Int. Ed., 2021, DOI: 10.1002/anie.202101628

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- Operando UV-vis powered by in situ EPR
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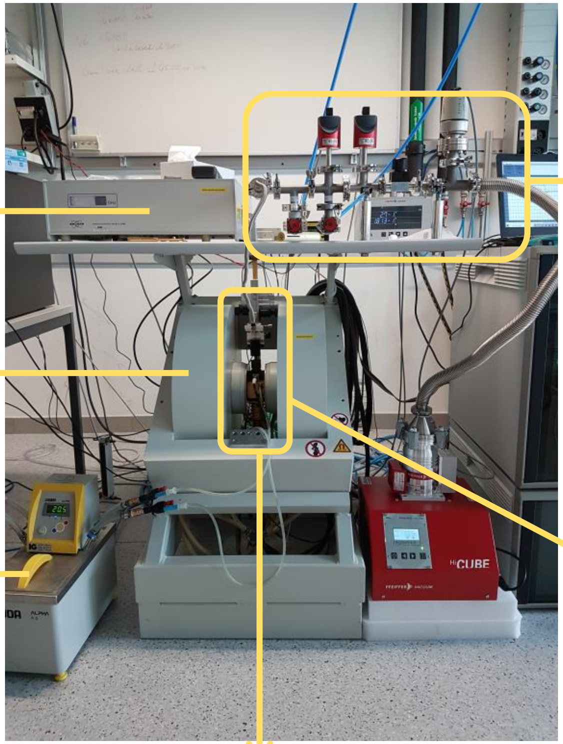
Operando EPR setup

Microwave bridge (Bruker)

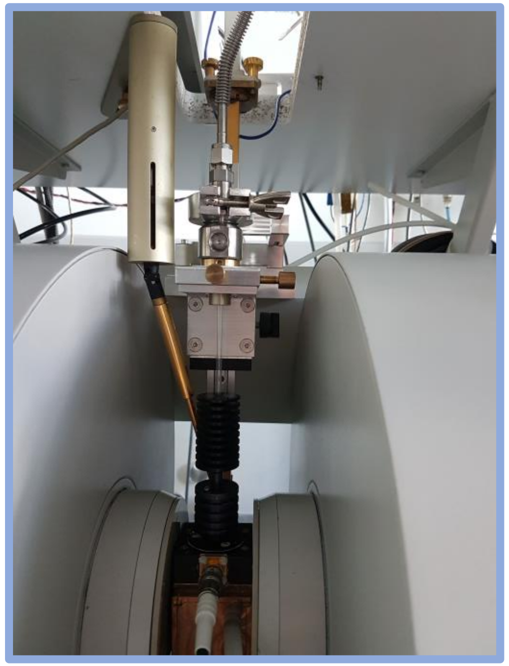
Electromagnet up to 0.7 T

Water cooling for the high temperature Resonator



Gas supply system

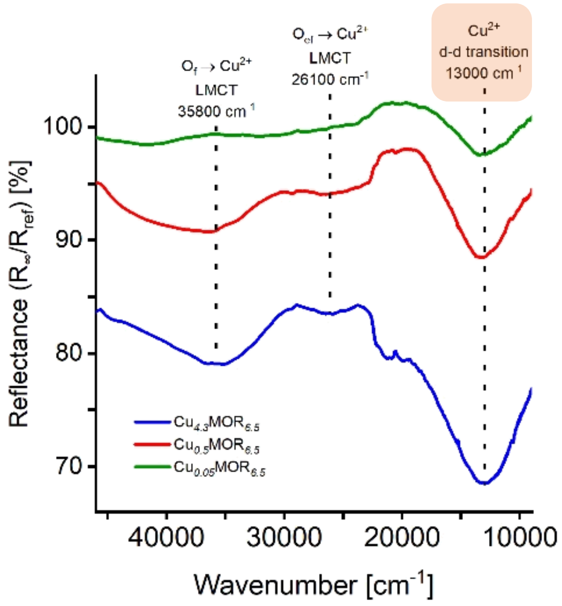
Home build high-temperature resonator from r.t. to 773 K



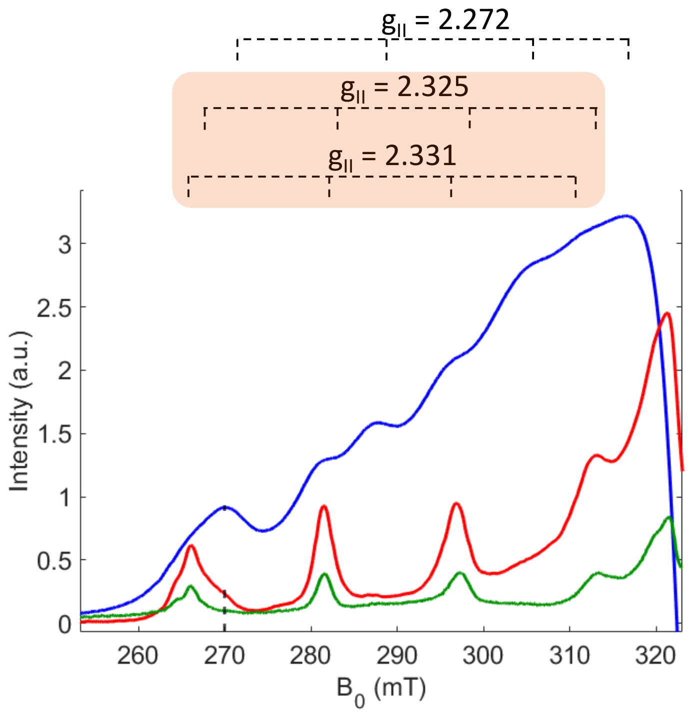
In Situ UV-Vis DRS and EPR Spectra of Activated Materials

- 13000 cm^{-1}: d-d transition of bare, isolated Cu^{2+}
- 26100 cm^{-1}: LMCT transition of $[Cu_2(\mu\text{-}O)]^{2+}$
  - Present only above Cu/Al ratio of 0.29

- 2.325 & 2.331: bare Cu^{2+} in different environments
- 2.272: Cu^{2+} charge balanced by one AlO_4 T-site
  - Presumably present as $[CuOH]^+$

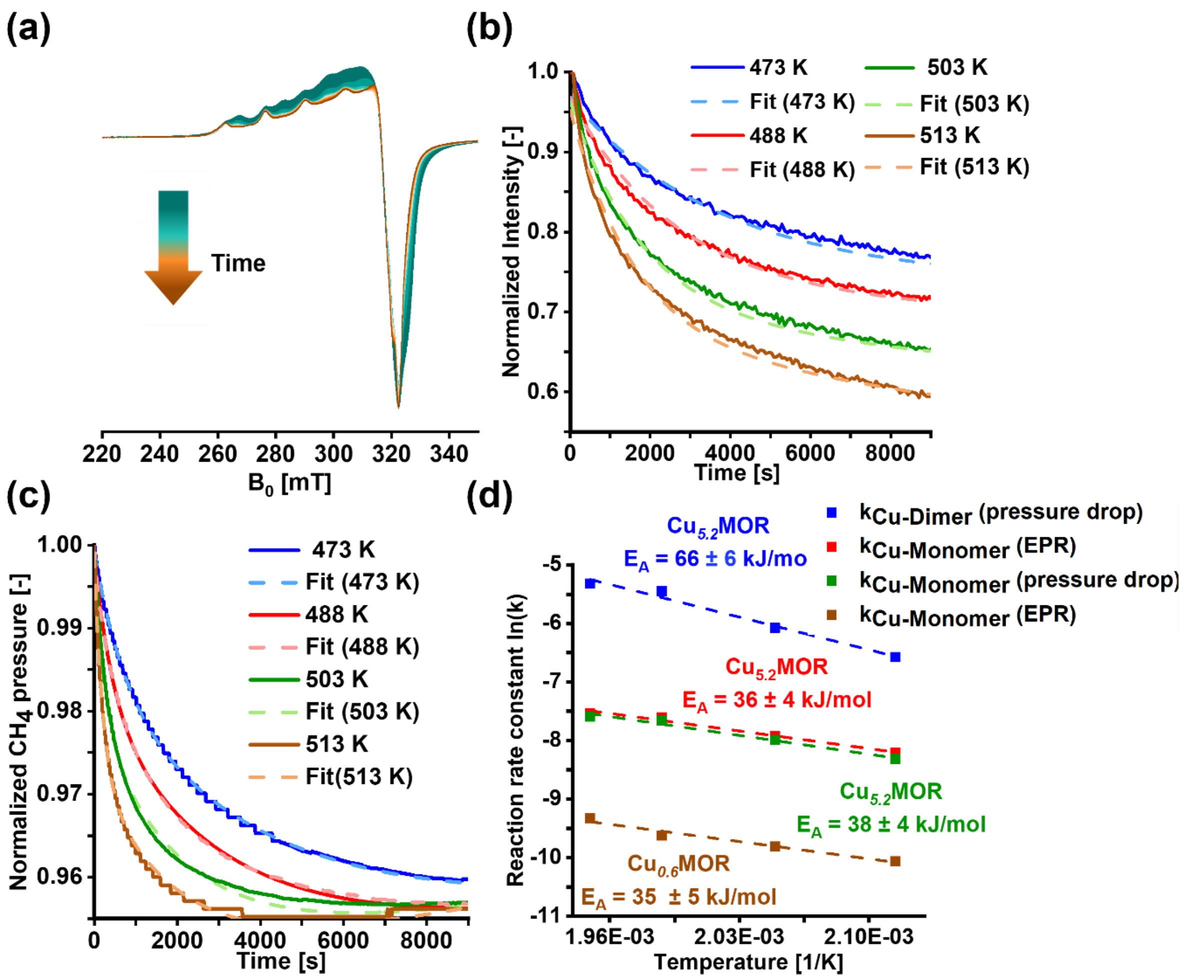


In situ UV-Vis DRS of activated $Cu_{4.3}MOR_{6.5}$ (blue), $Cu_{0.5}MOR_{6.5}$ (red), and $Cu_{0.05}MOR_{6.5}$ (green) measured against a Na-$MOR_{6.5}$ white standard.



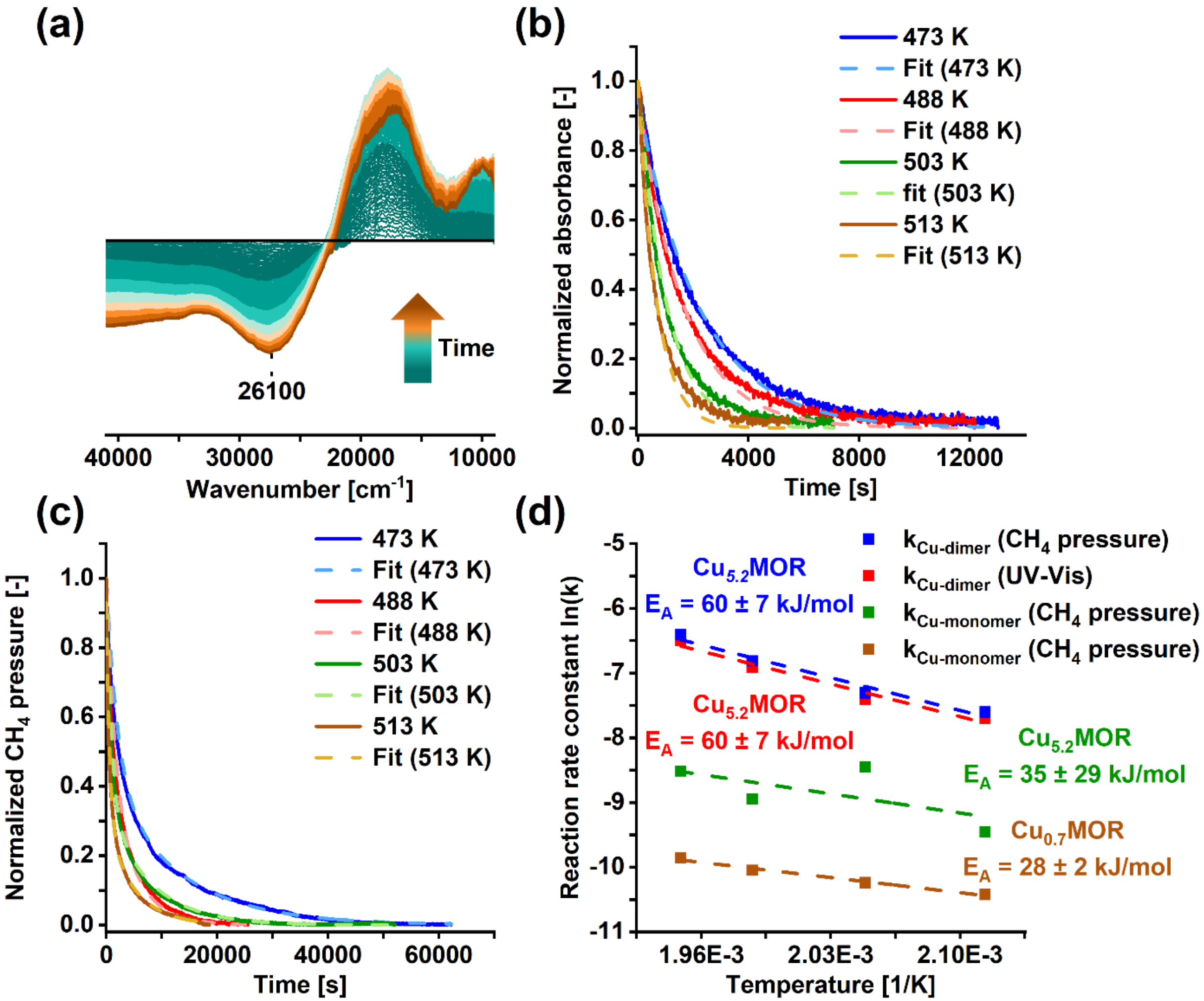
In situ X-band EPR spectra of activated $Cu_{4.3}MOR_{6.5}$ (blue), $Cu_{0.5}MOR_{6.5}$ (red), and $Cu_{0.05}MOR_{6.5}$ (green). Measured by Jörg W. A. Fischer (EPR Group, ETH Zurich).

Operando EPR and Kinetic Analysis



- Negative band at 27500 cm^{-1} on $Cu_{4.3}MOR_{6.5}$:consumption of $[Cu_2(\mu\text{-}O)]^{2+}$
- Negative band at 18200 cm^{-1} on $Cu_{0.5}MOR_{6.5}$ and $Cu_{0.05}MOR_{6.5}$ with shoulder at 20200 cm^{-1}: photoluminescence of Cu^+ and consumption of bare Cu^{2+}

Operando UV-Vis DRS and Kinetic Analysis



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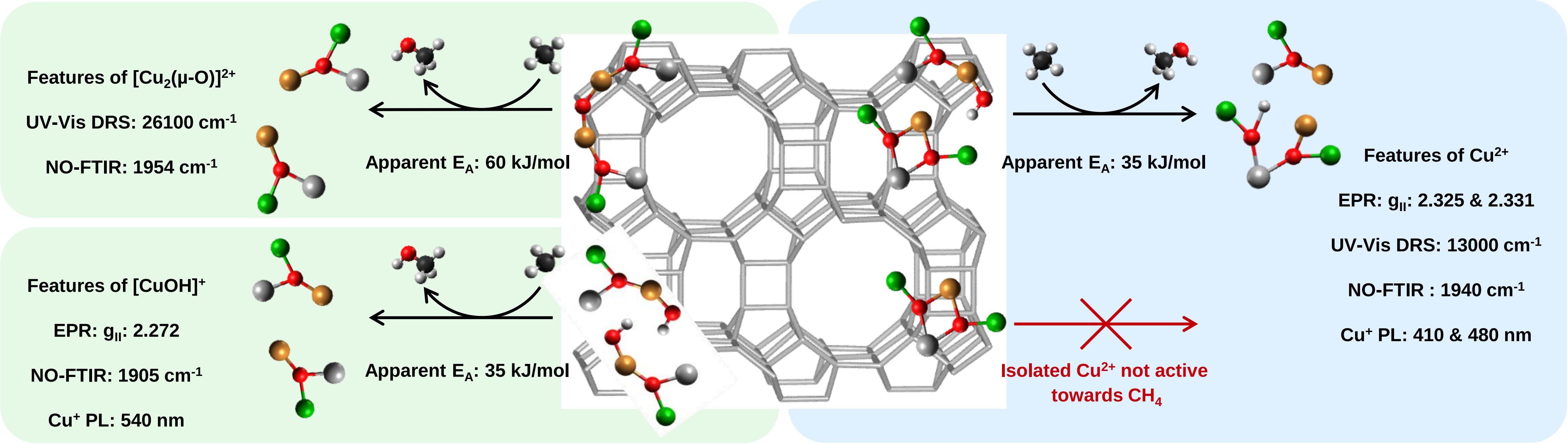
Methane Oxidation Pathways on Cu-MOR



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Take-home messages

- The importance of modern advanced physical chemical methods in studying solid-gas reactions can not be overestimated
- Look from both sides – active site and substrate carry important information about the mechanism of the (side) reactions
- Know the strong sides of each method to create strategy of the study
- Combine spectroscopy with kinetic studies to make analysis deeper and comprehensive: the unexpected behavior can be revealed