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Selective catalytic oxidation of propene over alkali modified transition metal catalysts

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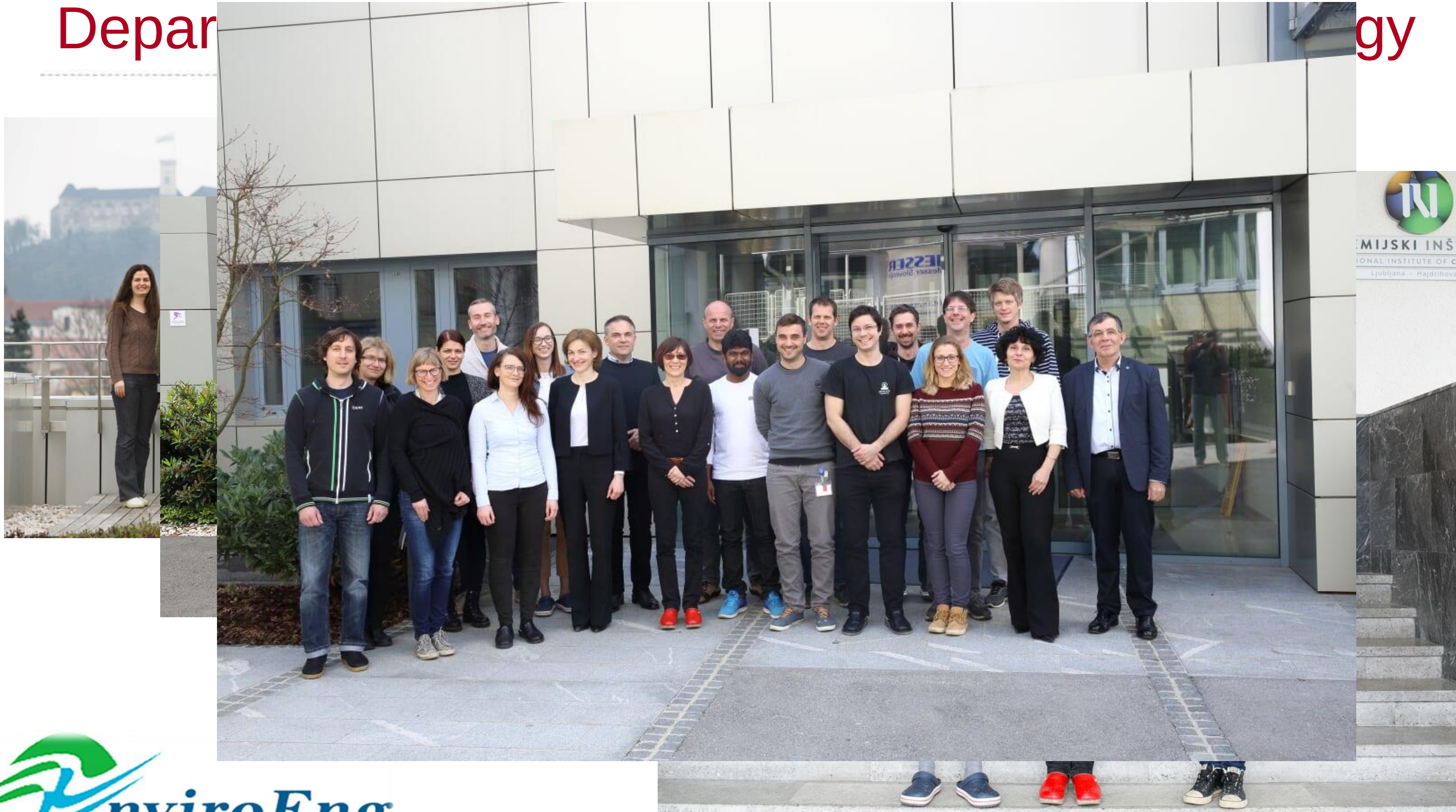

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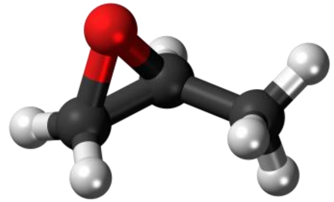
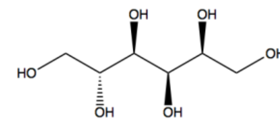
Propylene oxide

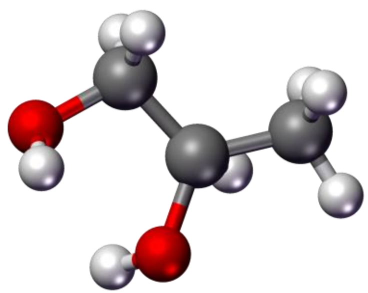


- production of polyether polyols by alkoxylation

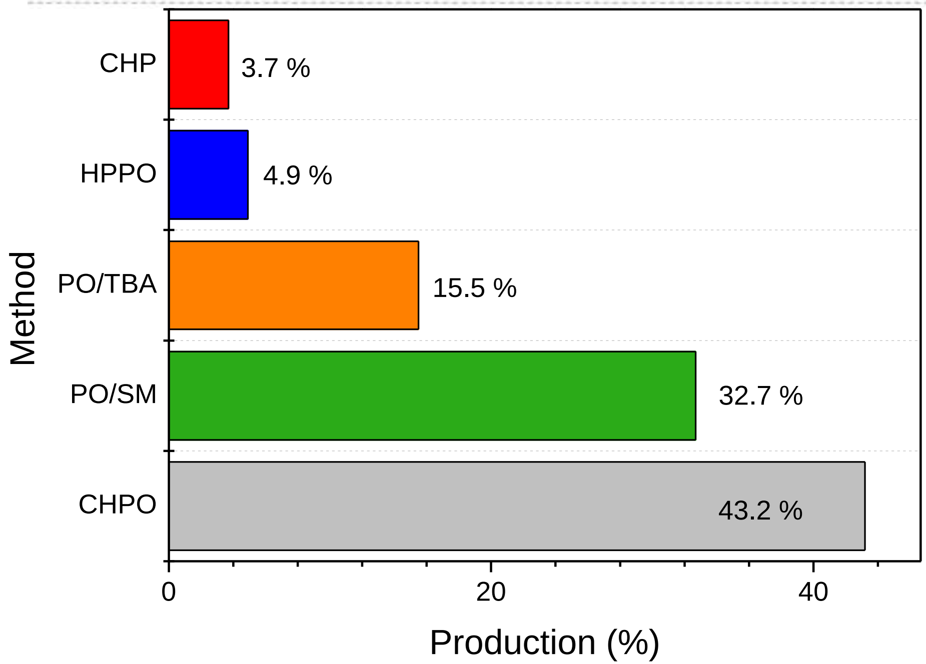


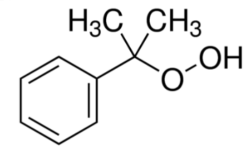
- for use in making polyurethane plastics

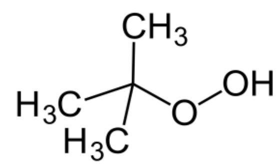
- also hydrolysed into propylene glycol

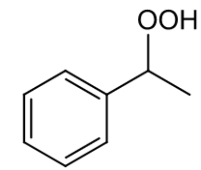


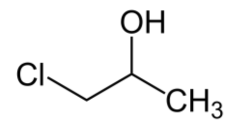
Production







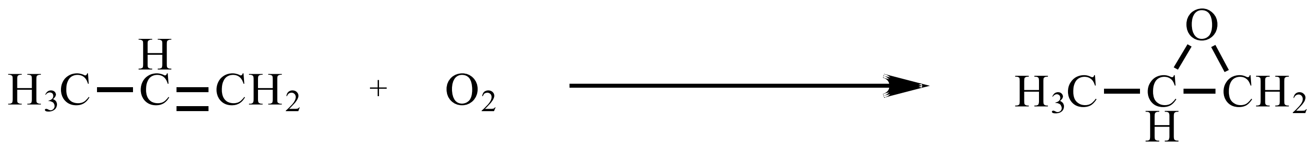




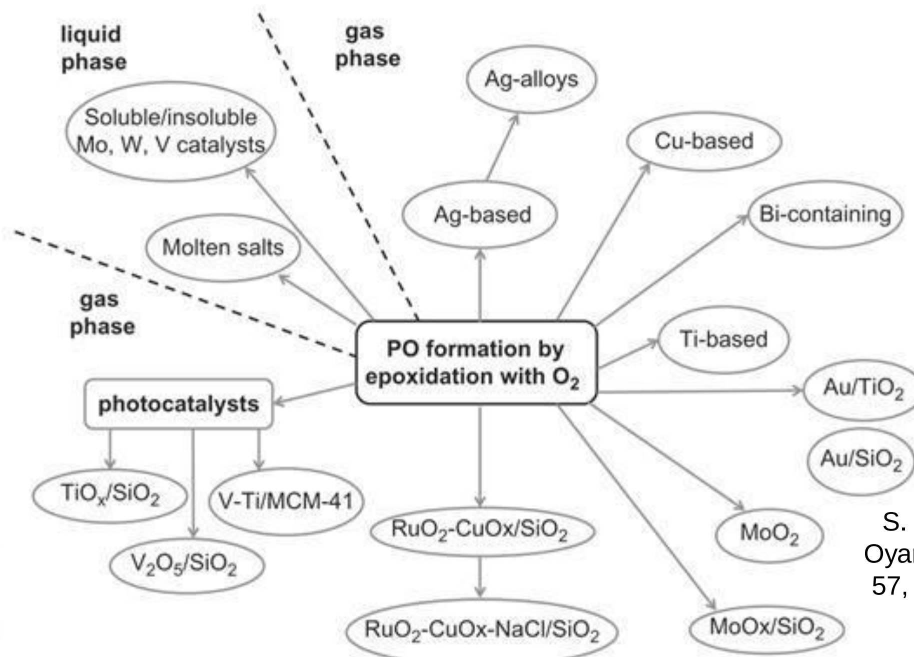
- the chlorohydrin and organic hydroperoxide processes

S. J. Khatib and S. T. Oyama, Catal. Rev., vol. 57, no. 3, pp. 306–344, 2015

Current work



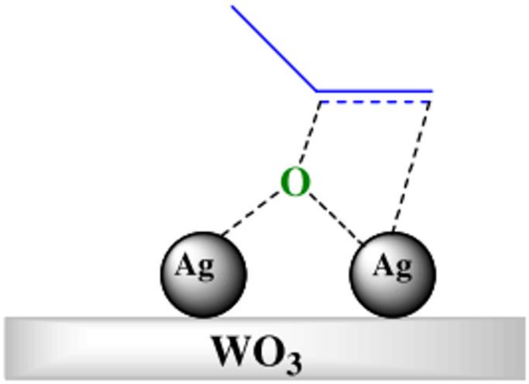
- with propylene recycling, a minimum PO selectivity should be 60-70% at a 10% conversion at 3000 h^{-1} gas hourly space velocity



S. J. Khatib and S. T. Oyama, Catal. Rev., vol. 57, no. 3, pp. 306–344, 2015

Review

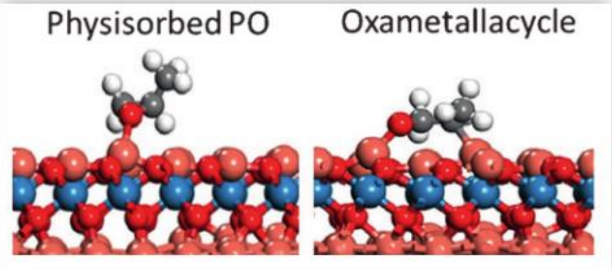
- commercial application is still out of reach
- a necessary intermediate is the oxametallacycle
- bond lengths/strength (Me-O versus Me-C) have a significant impact on selectivity



S. Ghosh, S. S. Acharyya, R. Tiwari, B. Sarkar, R. K. Singha, C. Pendem, T. Sasaki, and R. Bal, ACS Catal., vol. 4, no. 7, pp. 2169–2174, 2014.

S. J. Khatib and S. T. Oyama, Catal. Rev., vol. 57, no. 3, pp. 306–344, 2015

Materials and Methods



- According to the literature Cu containing catalysts are very promising in propylene epoxidation
- CuO loaded SiO_2 (silica gel) was prepared by incipient wetness impregnation and tested for its catalytic activity
- Based on this preliminary testing copper oxide on silica produced trace amounts of propylene oxide
- The goal was to prepare highly dispersed copper species

Dilution hydrolysis technique

- The appropriate amount of copper nitrate was dissolved in deionized water (weight loadings 1-10%)
- After complete dissolution, KIT-6 was added and the pH adjusted to approximately 9
- Hydrolysis of the copper ammonia complex was achieved by dilution with deionized water
- The precipitate was washed with centrifugation and dried at 80 °C fo 5 h, and calcined at 350 °C (2 °C min^{-1} to 350 °C, hold for 3 h)

Alkali modification of the catalyst

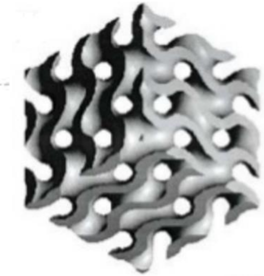
- The appropriate amount of alkali or earth alkali nitrate was dissolved in deionized water (final concentration 0.1 M, 0.05 M for calcium nitrate)

- After complete dissolution, the copper loaded KIT-6 was added

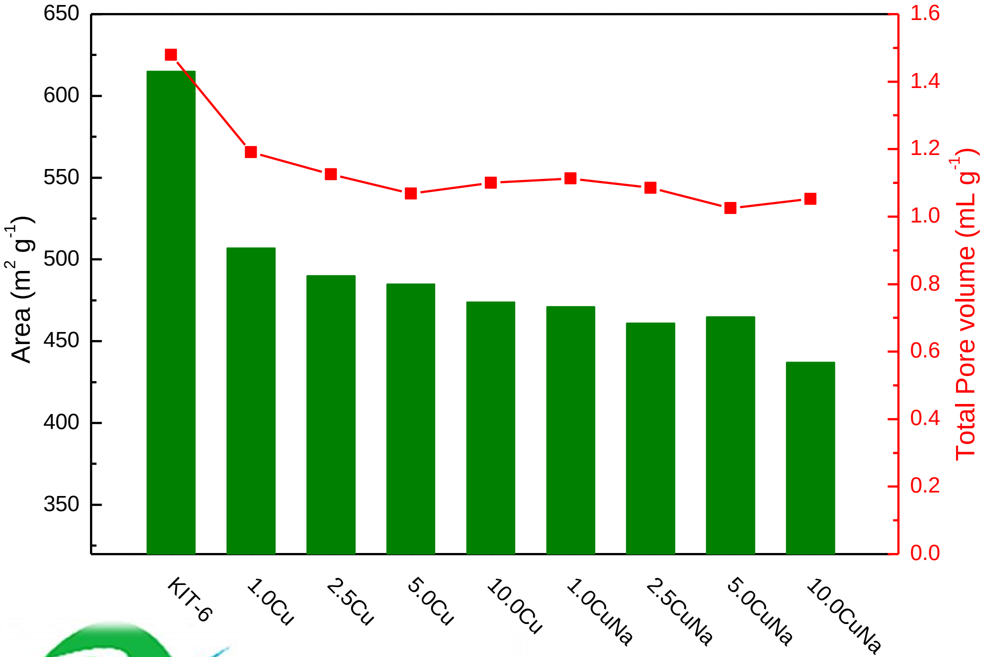
- The suspension was stirred for 3 h

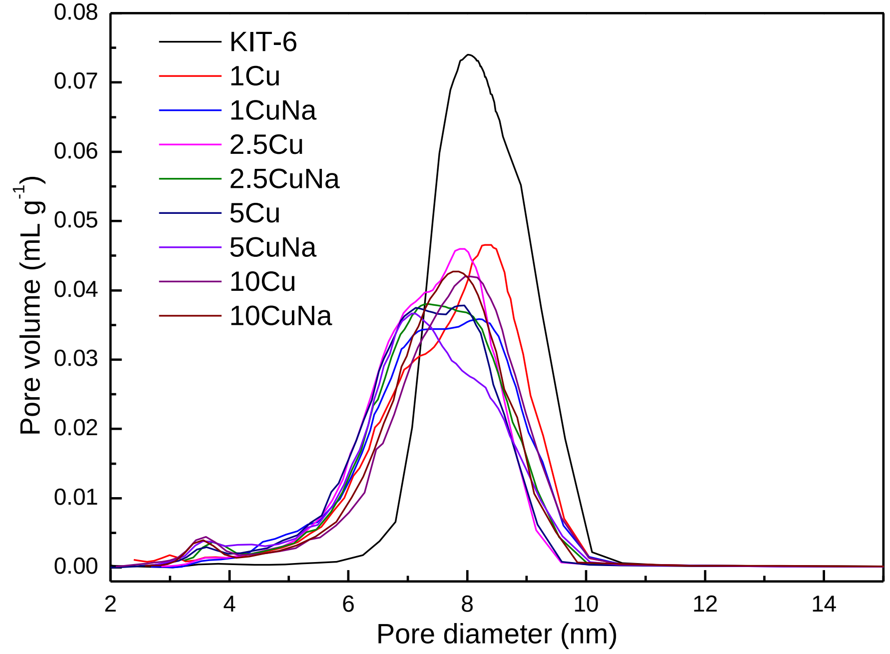
- The precipitate was washed with centrifugation and dried at 80 °C fo 5 h, and calcined at 350 °C (2 °C min^{-1} to 350 °C, hold for 3 h)

N_2 sorption analysis



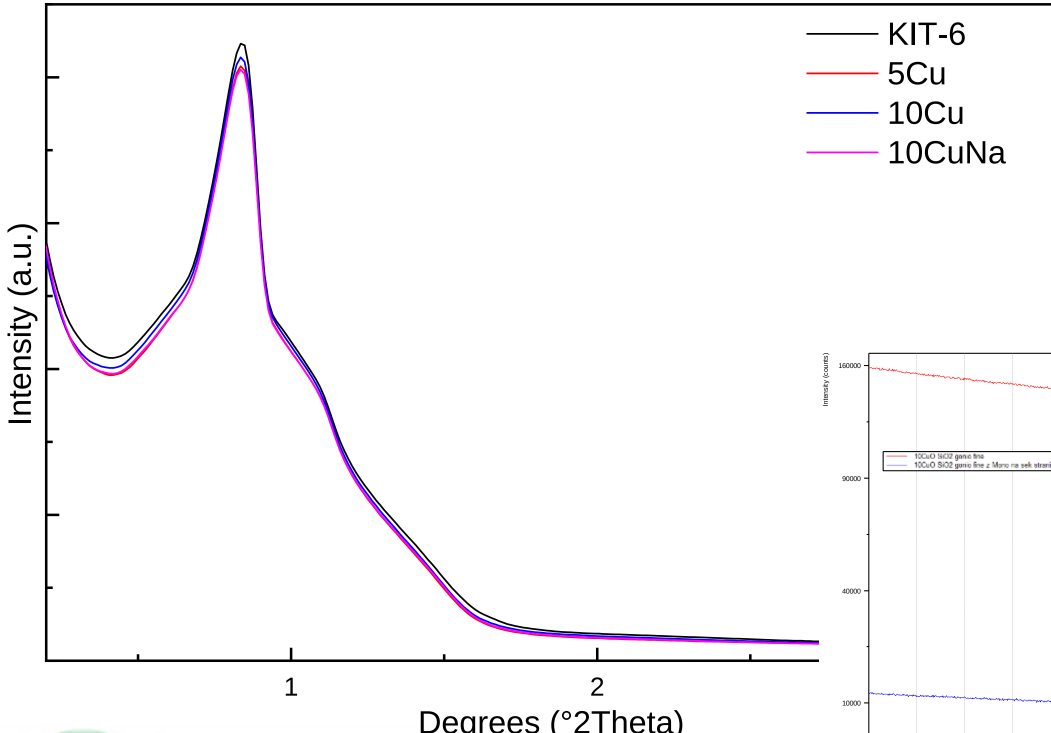
- Specific surface area and pore distribution was measured to see the effect of copper loading on structure



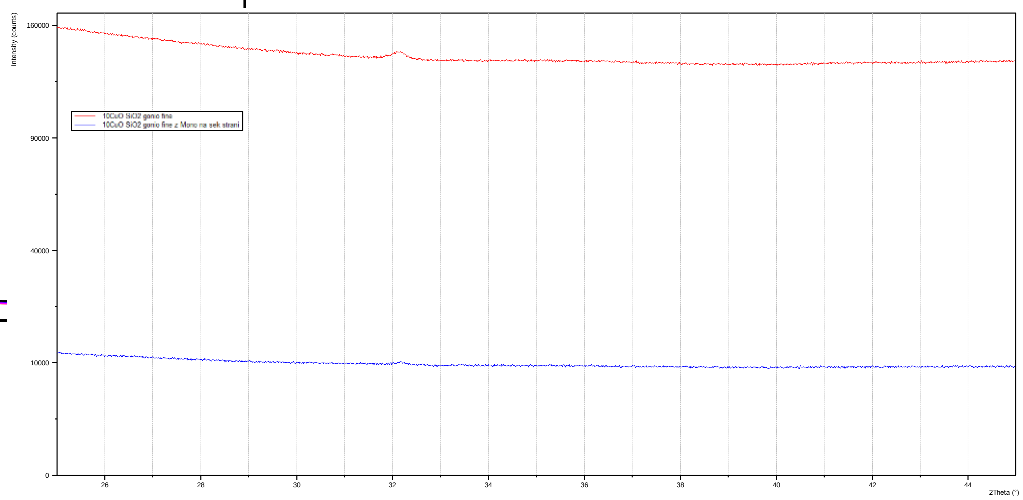


XRD

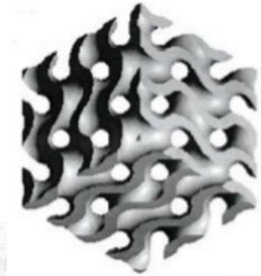
- Mesoporous ordering is not affected by copper loading

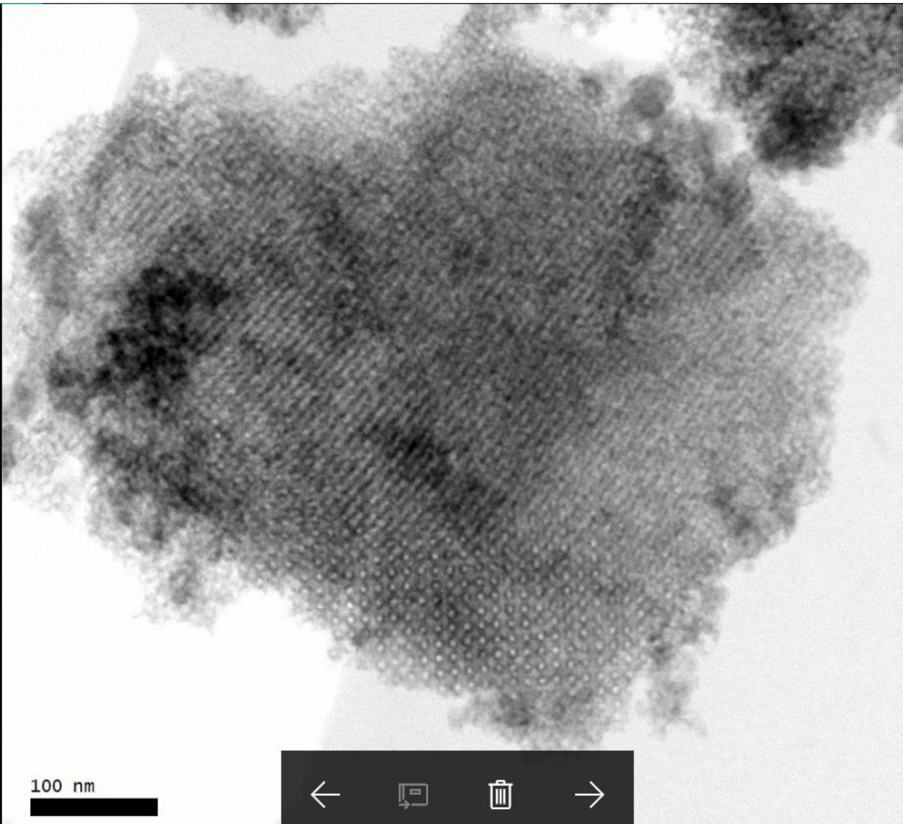


- No crystalline copper species

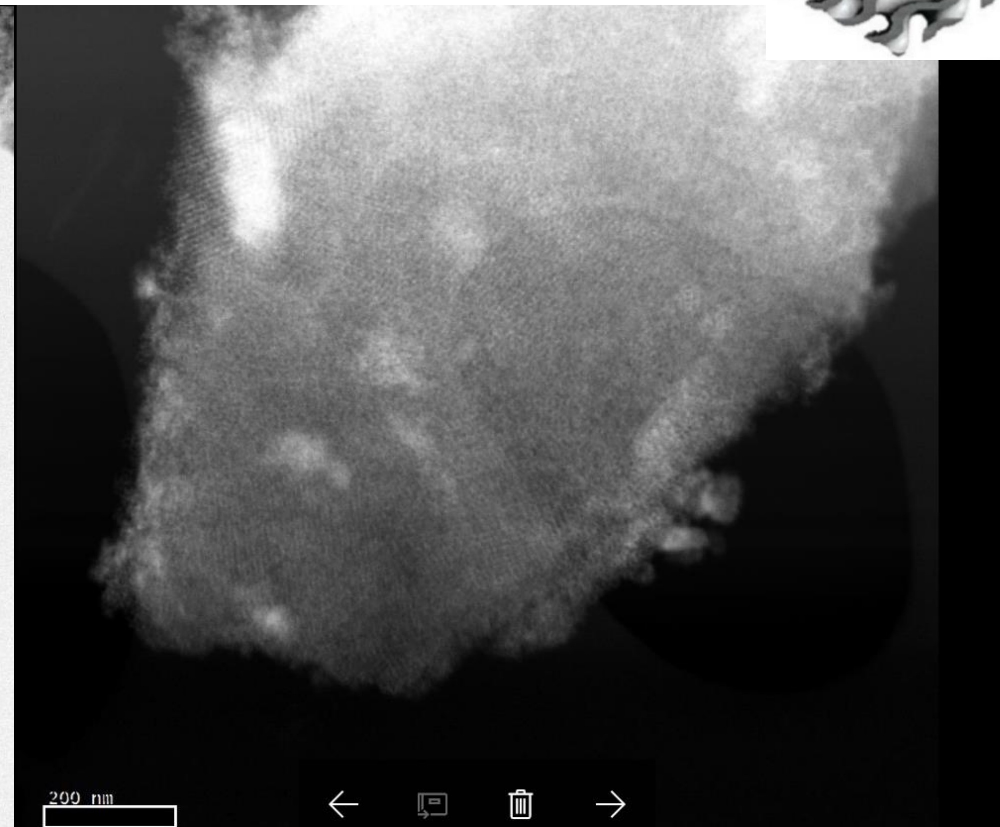


TEM analysis



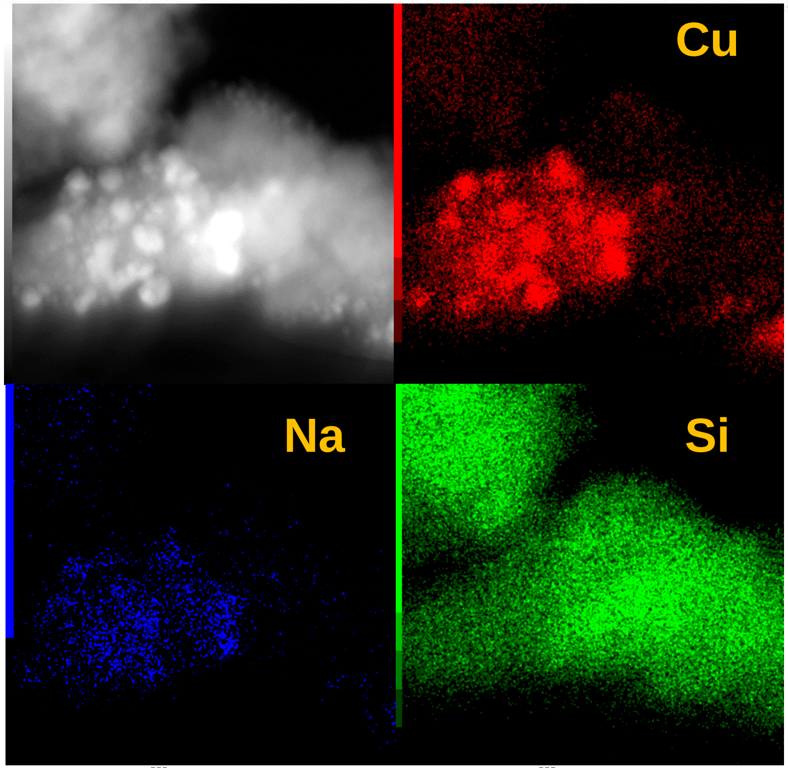


BF-STEM image of the SiOx matrix showing the mesoporous ordering

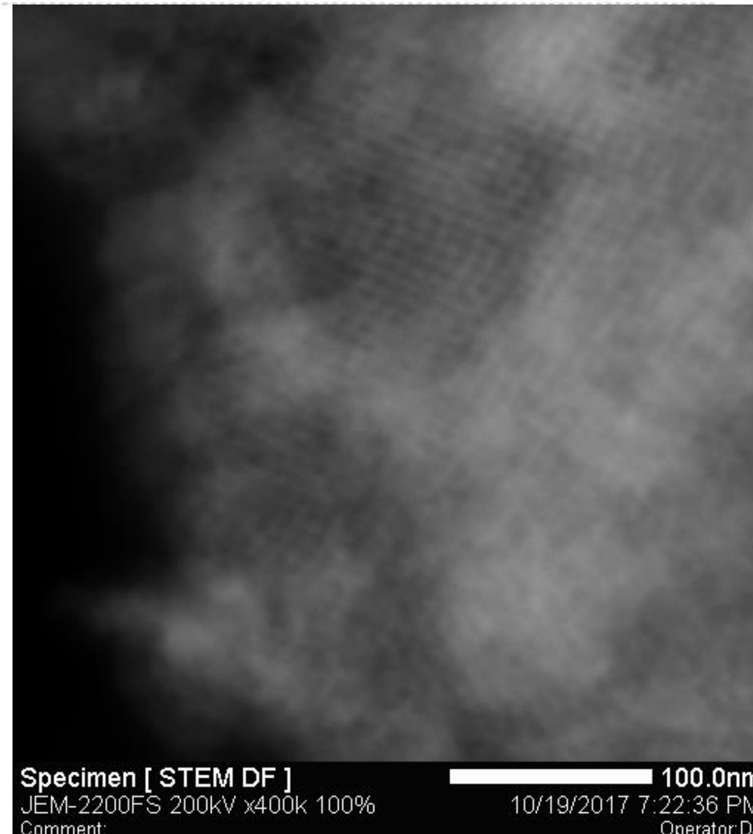


HAADF-STEM showing “mass distribution” in the sample, the lighter part is copper

TEM analysis



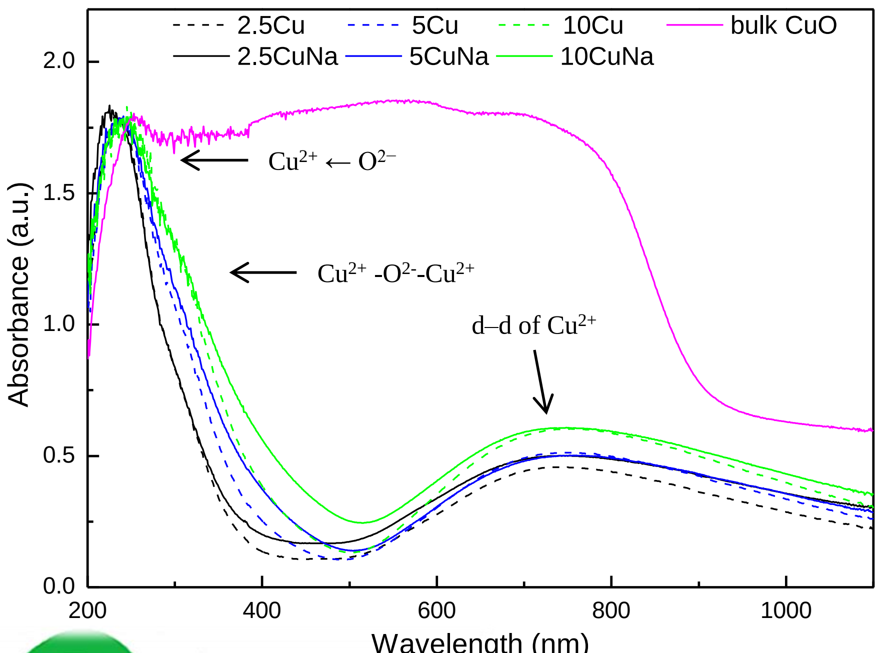
TEM-EDS mapping for sample10CuNa

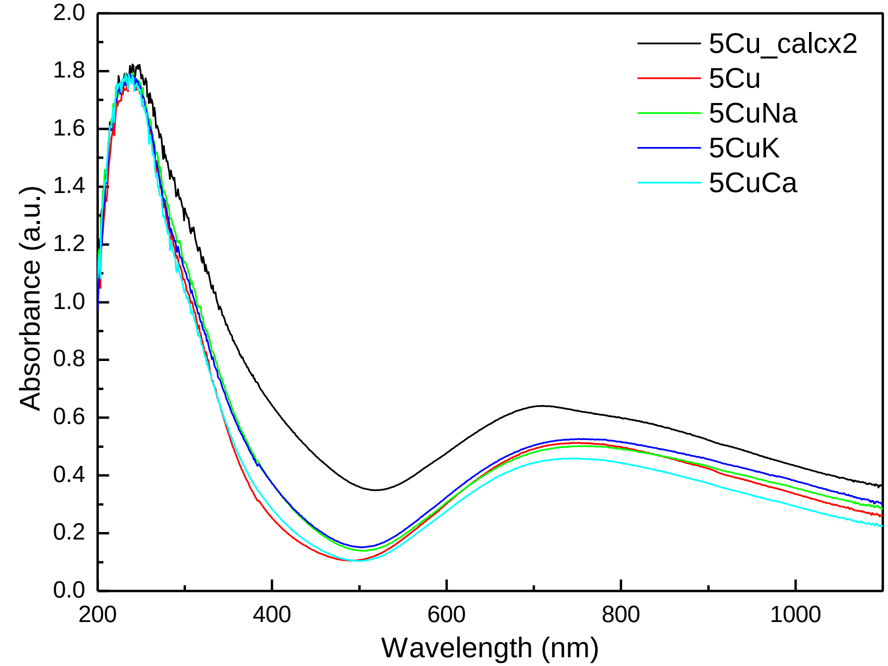


Damage on silica framework after only minutes of exposure

UV/VIS DR analysis

- The graphs below are normalized to the peak at approximately 240 nm
- Alkali and earth alkali prevent deactivation as a result of sintering

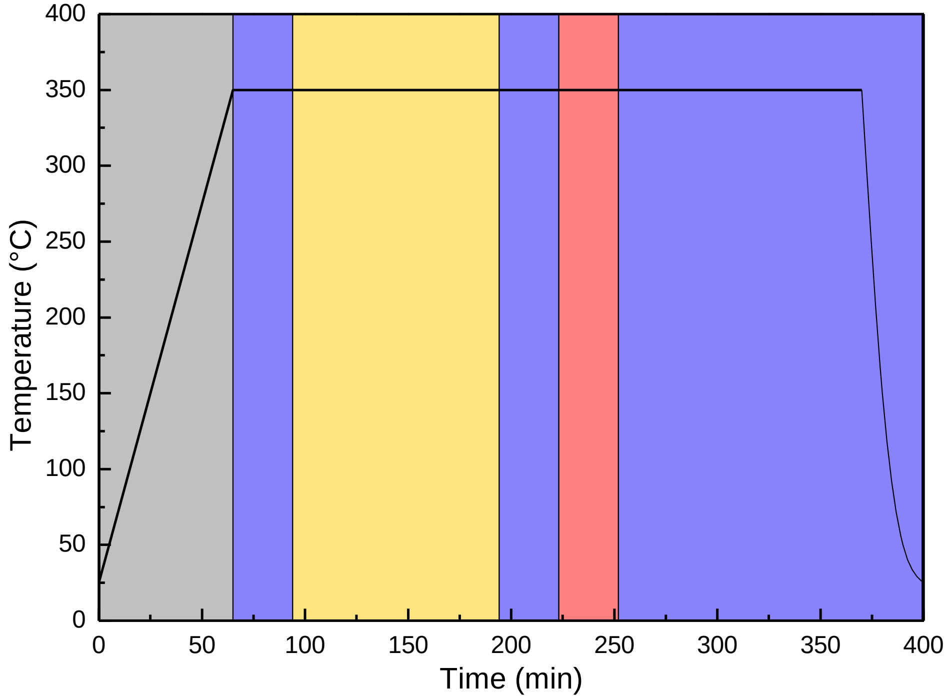




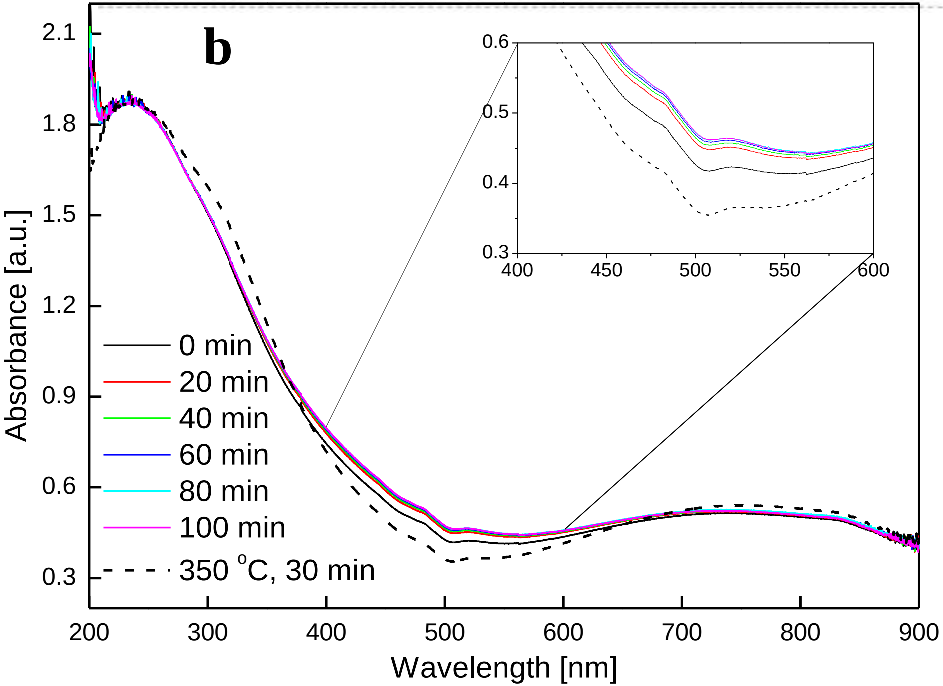
H. Praliaud, S. Mikhailenko, Z. Chajar, M. Primet, Appl. Catal., B, vol. 16, no. 4, pp. 359–374, 1998

5Cu *in situ* UV/VIS

- Grey area: 20% oxygen in helium, heating ramp 5°C min^{-1}
- Blue area: 20% oxygen in helium, isothermal 350°C
- Yellow area: 16.67% oxygen and 16.67% propylene in helium, isothermal 350°C
- Red area: pure propylene, isothermal 350°C



5CuNa *in situ* UV/VIS



5CuNa during propene oxidation

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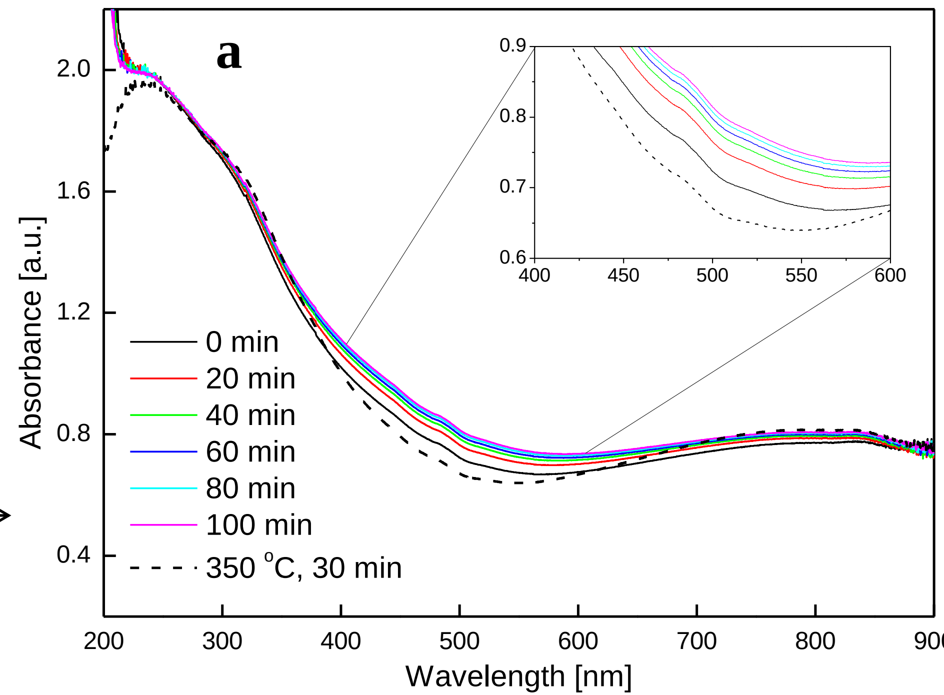

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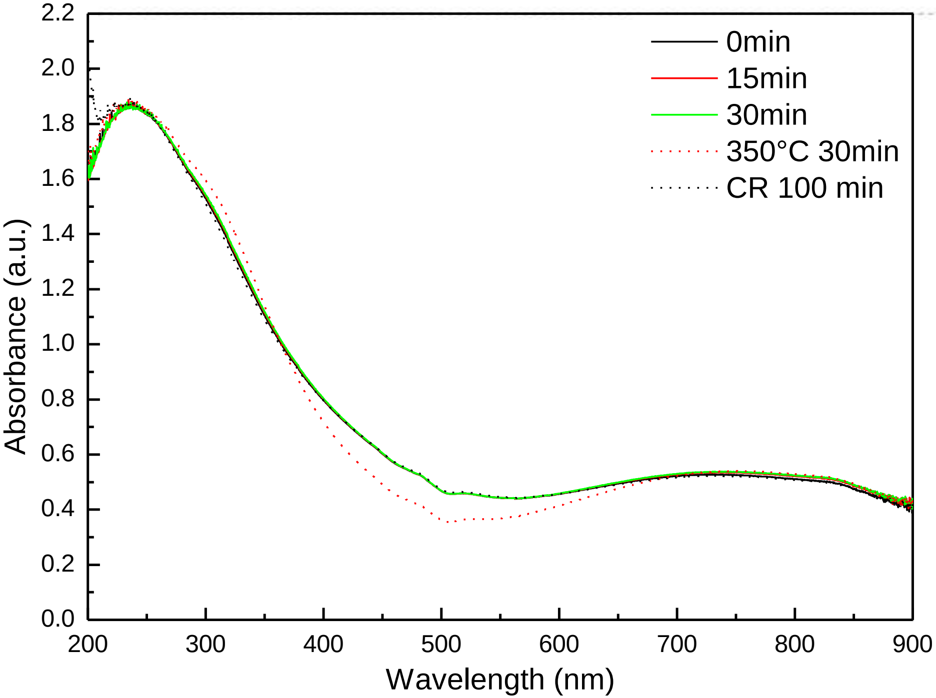
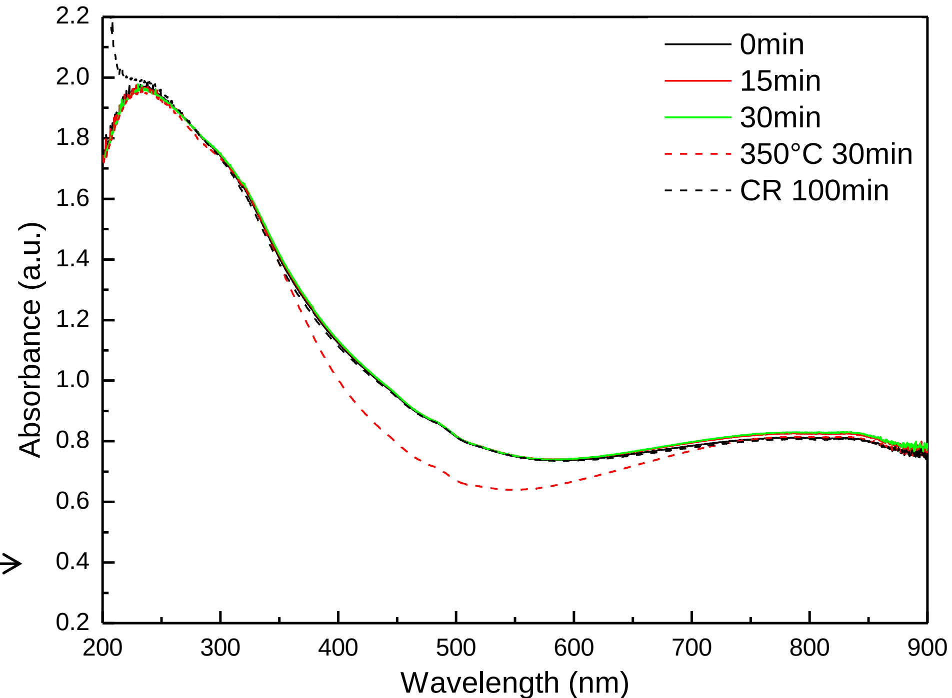
5CuNa *in situ* UV/VIS



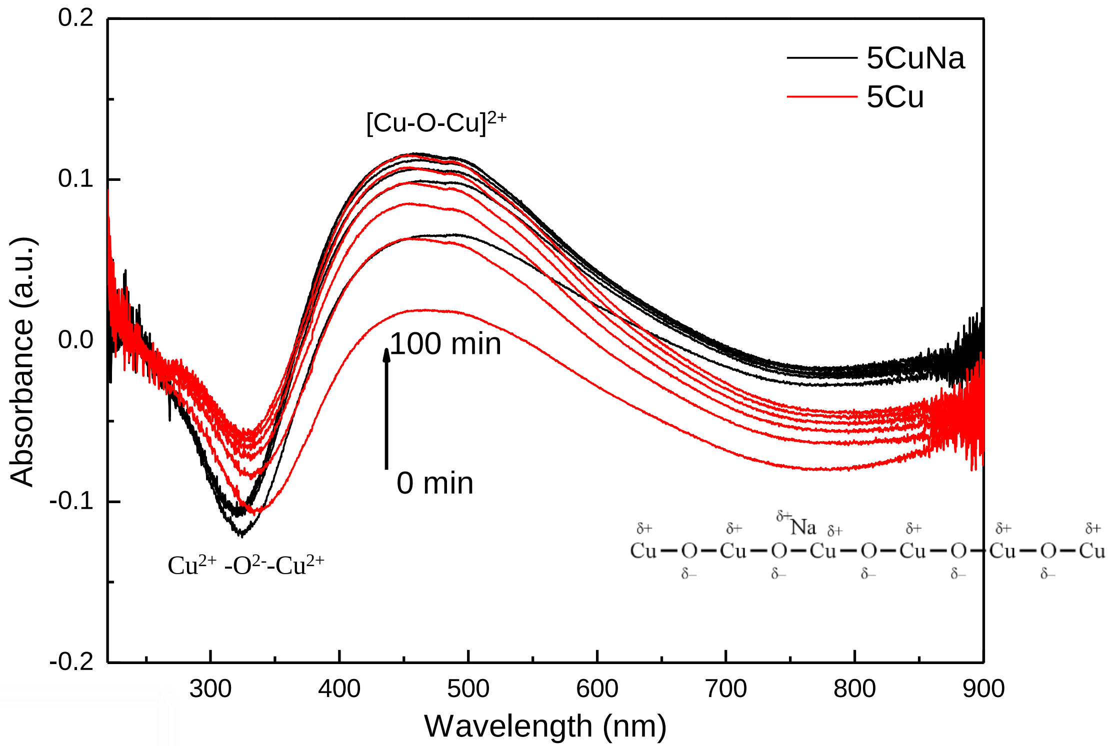
5CuNa during reoxidation after catalysis

5Cu during reoxidation after catalysis



5CuNa *in situ* UV/VIS

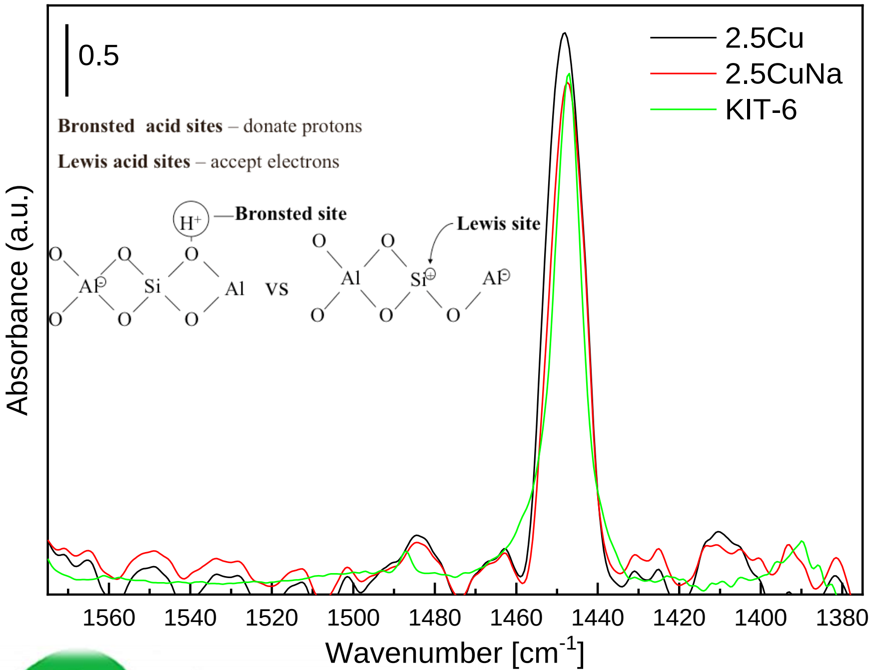
- Differential spectra; spectra after pretreatment were substracted from spectra after 100 min of catalysis

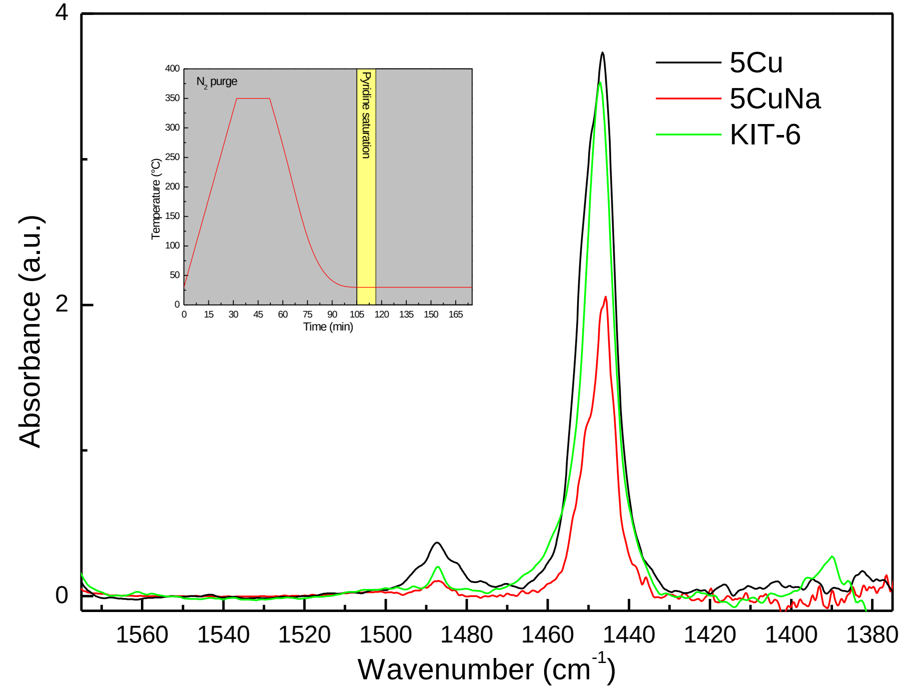


M. Zabilskiy, P. Djinović, B. Erjavec, G. Dražić, A. Pintar, Appl. Catal., B, vol. 163, pp. 113–122, 2015

Pyridine FTIR

- No Brønsted Acidity
- Lewis acidity reduces only with alkali modification





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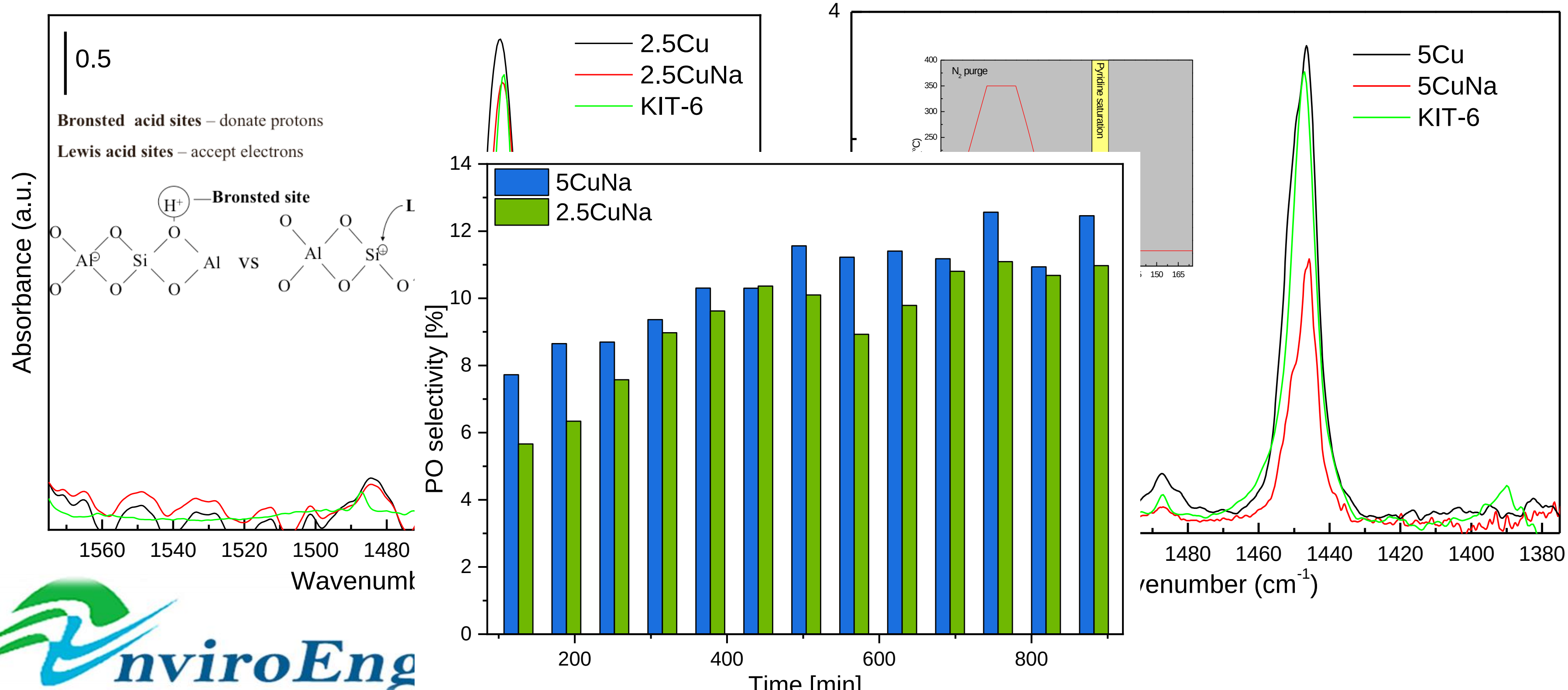
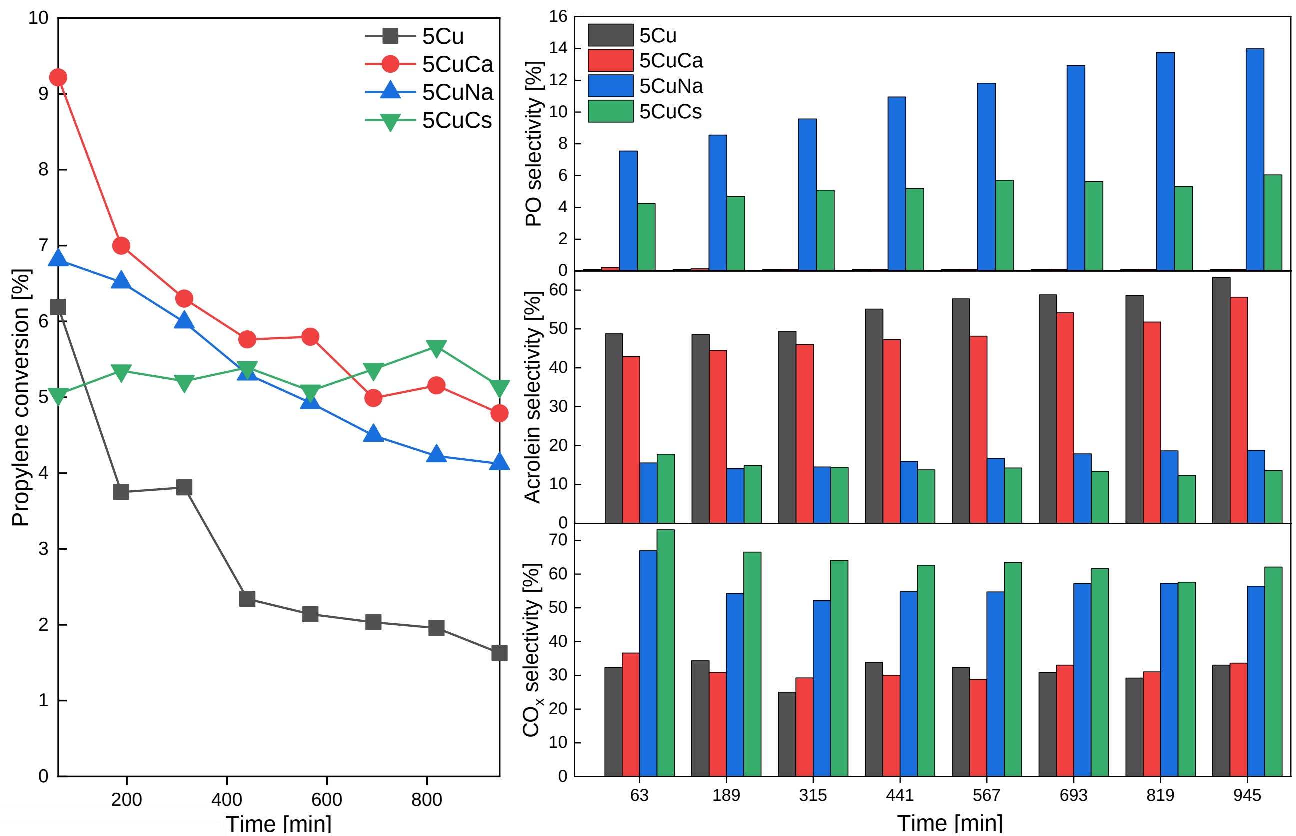
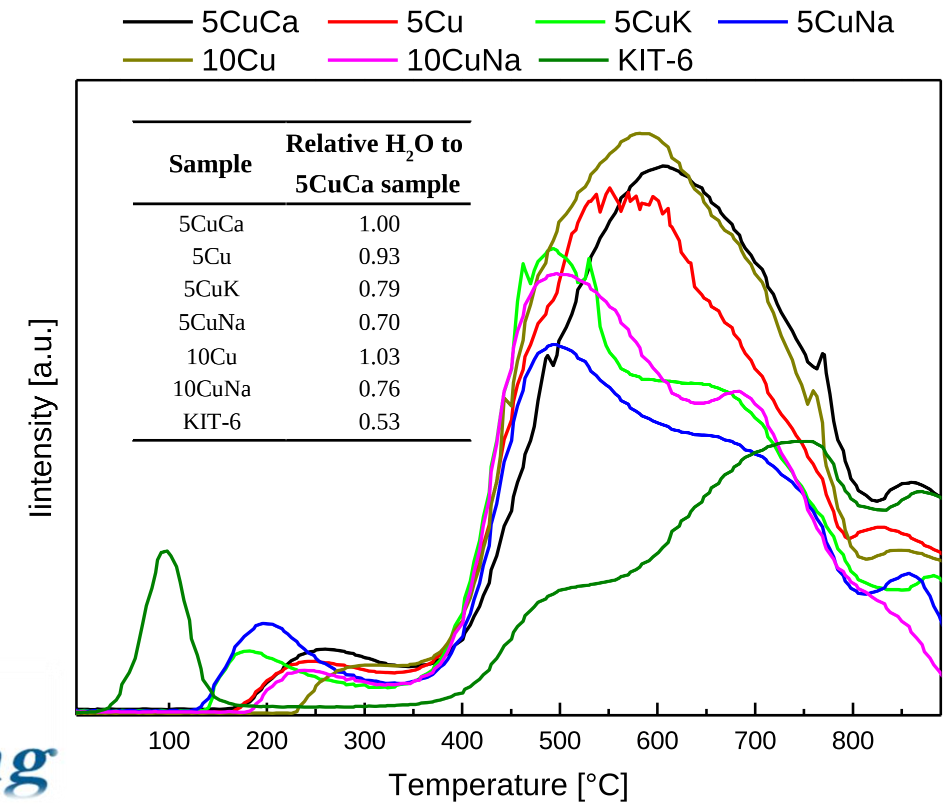


Catalytic tests



H_2O-TPD

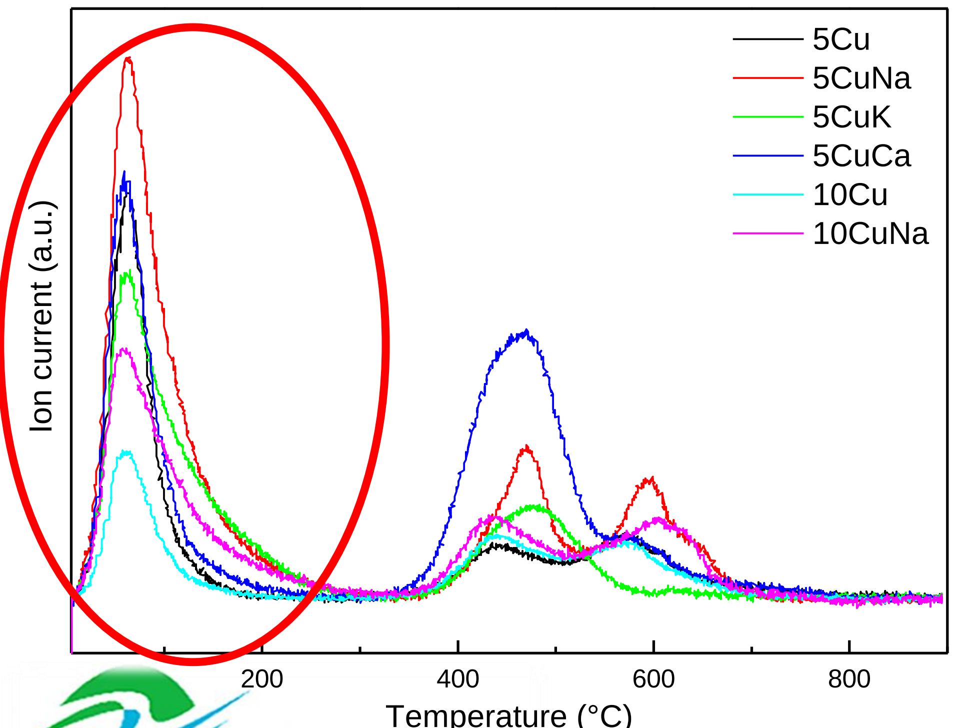
- Minimal similarity in the desorption profiles
- Low temperature peaks indicate weakly bound hydroxyl species



Sample	Relative H_2O to 5CuCa sample
5CuCa	1.00
5Cu	0.93
5CuK	0.79
5CuNa	0.70
10Cu	1.03
10CuNa	0.76
KIT-6	0.53

CO_2-TPD

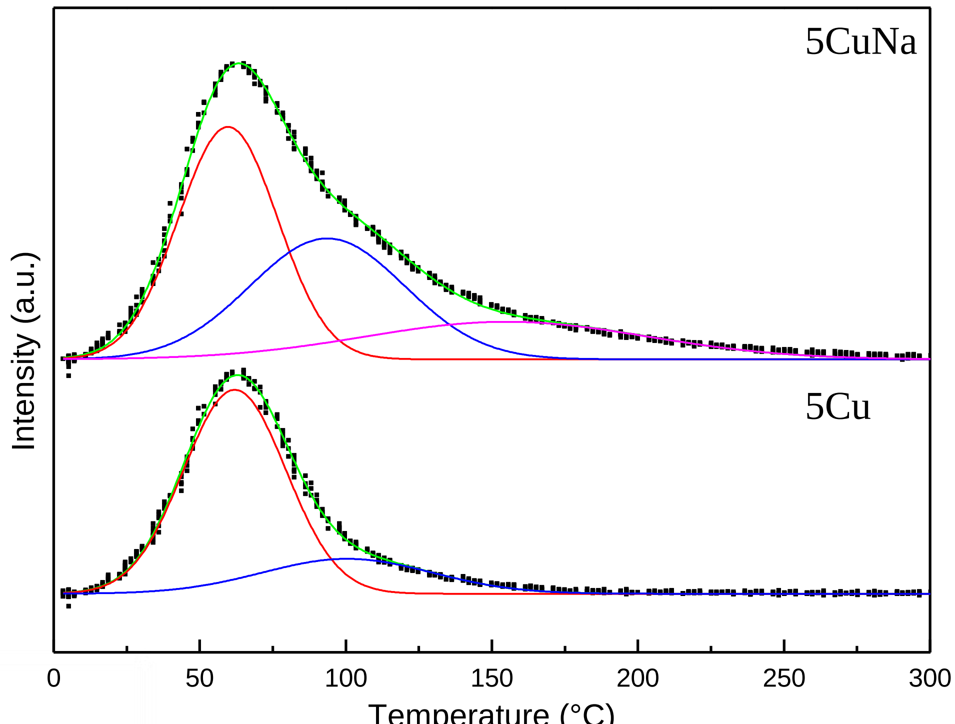
- Alkali and earth alkali modification adds basic sites to the surface
- Alkali modification induces shoulder formation in low temperature peaks



Desorbed CO_2 (mmol g_{Cu}^{-1})			
	Low T peak	High T peak	Peak at 155°C
5CuNa	2.6	1.3	0.52
5Cu	1.2	0.8	0
5CuCa	1.5	2.1	0
5CuK	2	0.7	0.64
10CuNa	1.5	1.1	0.42
10Cu	0.7	0.9	0

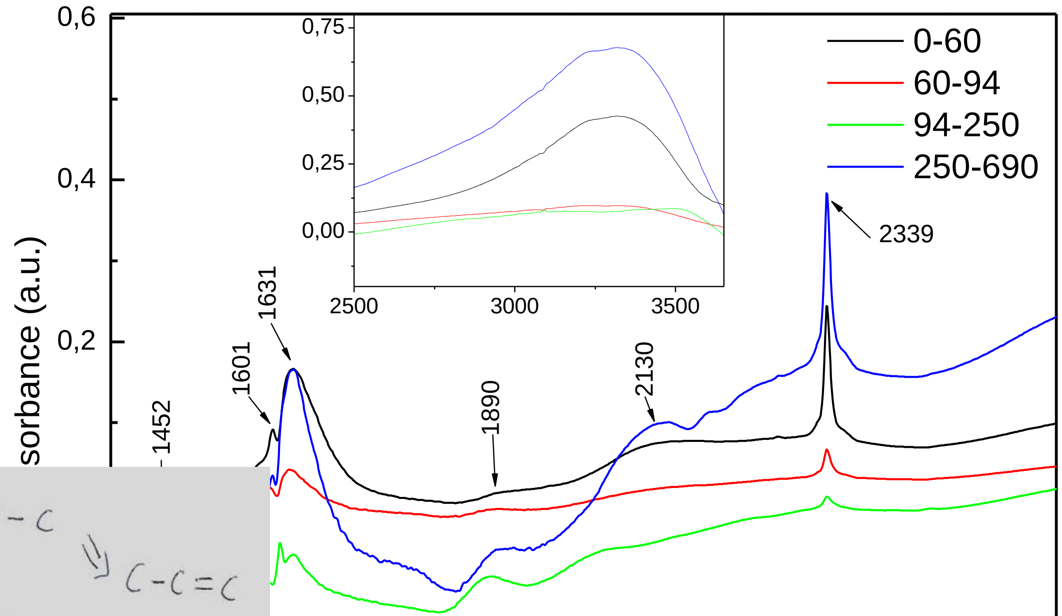
CO_2-TPD low T peak deconvolution

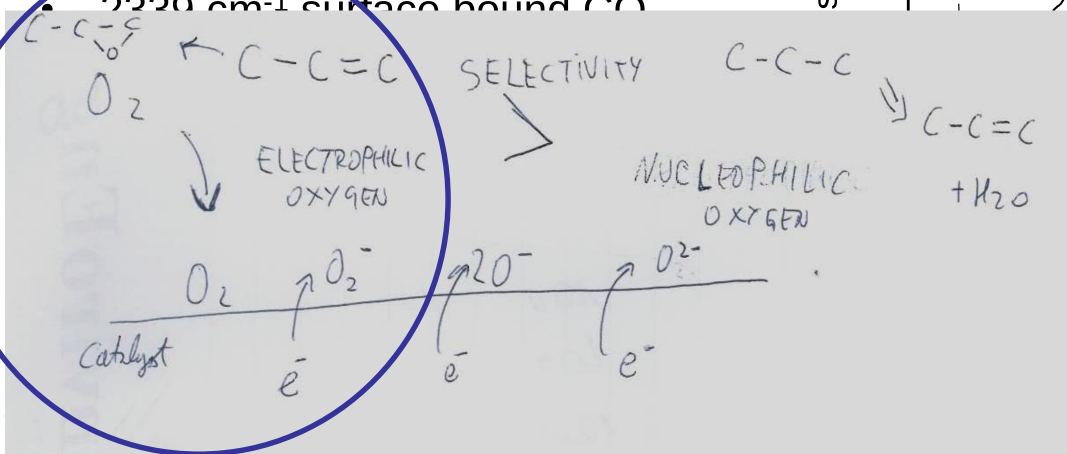
- Low temperature peak deconvolution shows 3 separate peaks
- Peak at 150 °C apparent only in alkali modified catalysts

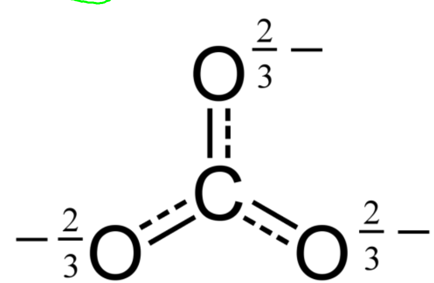


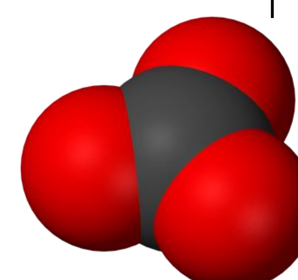
5CuNa CO_2-TPD measured with FTIR

- 1452 cm^{-1} ionic carbonate species
- 1601 cm^{-1} surface bound hydroxyls
- 1630 cm^{-1} surface bound hydroxyls
- 1890 cm^{-1} trace nitrates
- 2130 cm^{-1} monoxide species
- 2339 cm^{-1} surface bound CO









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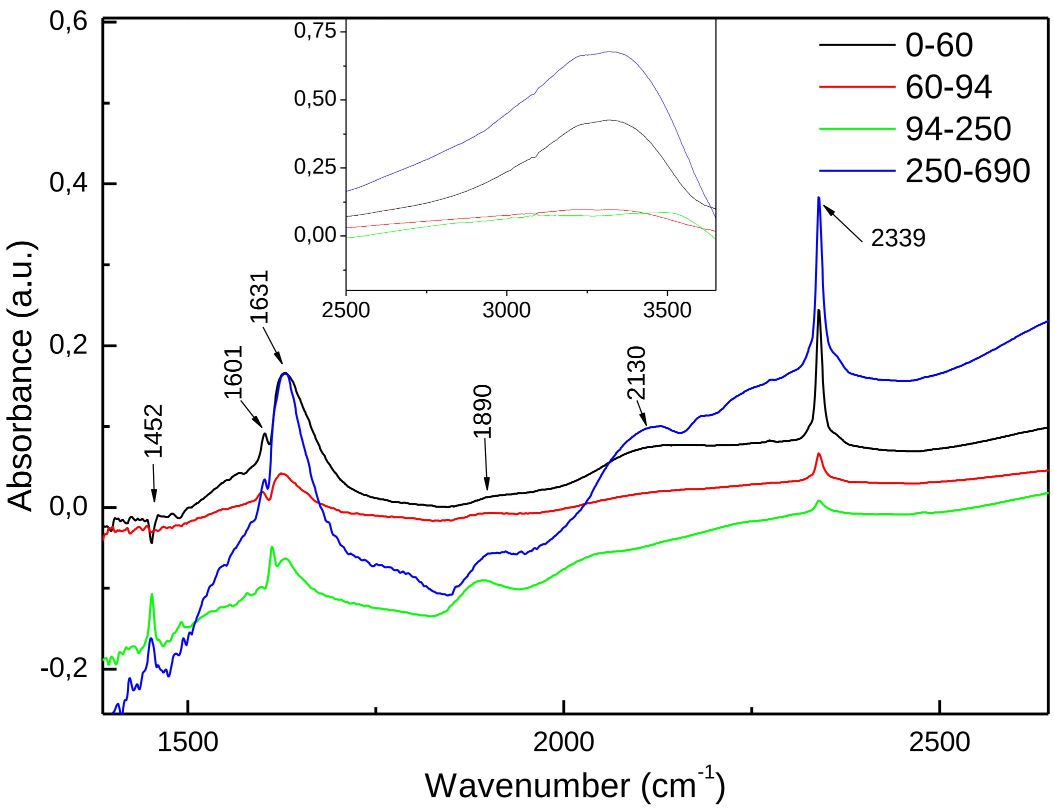
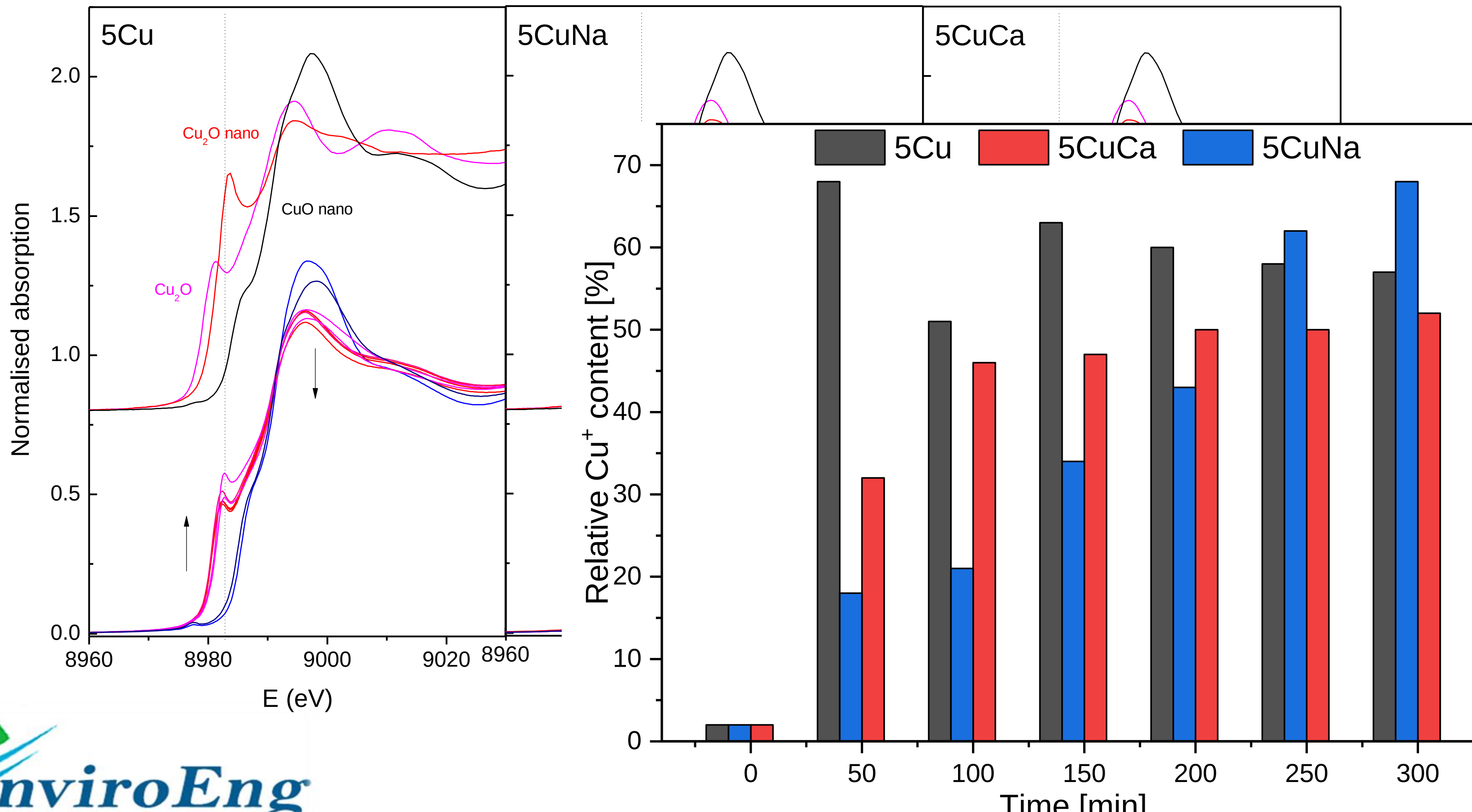
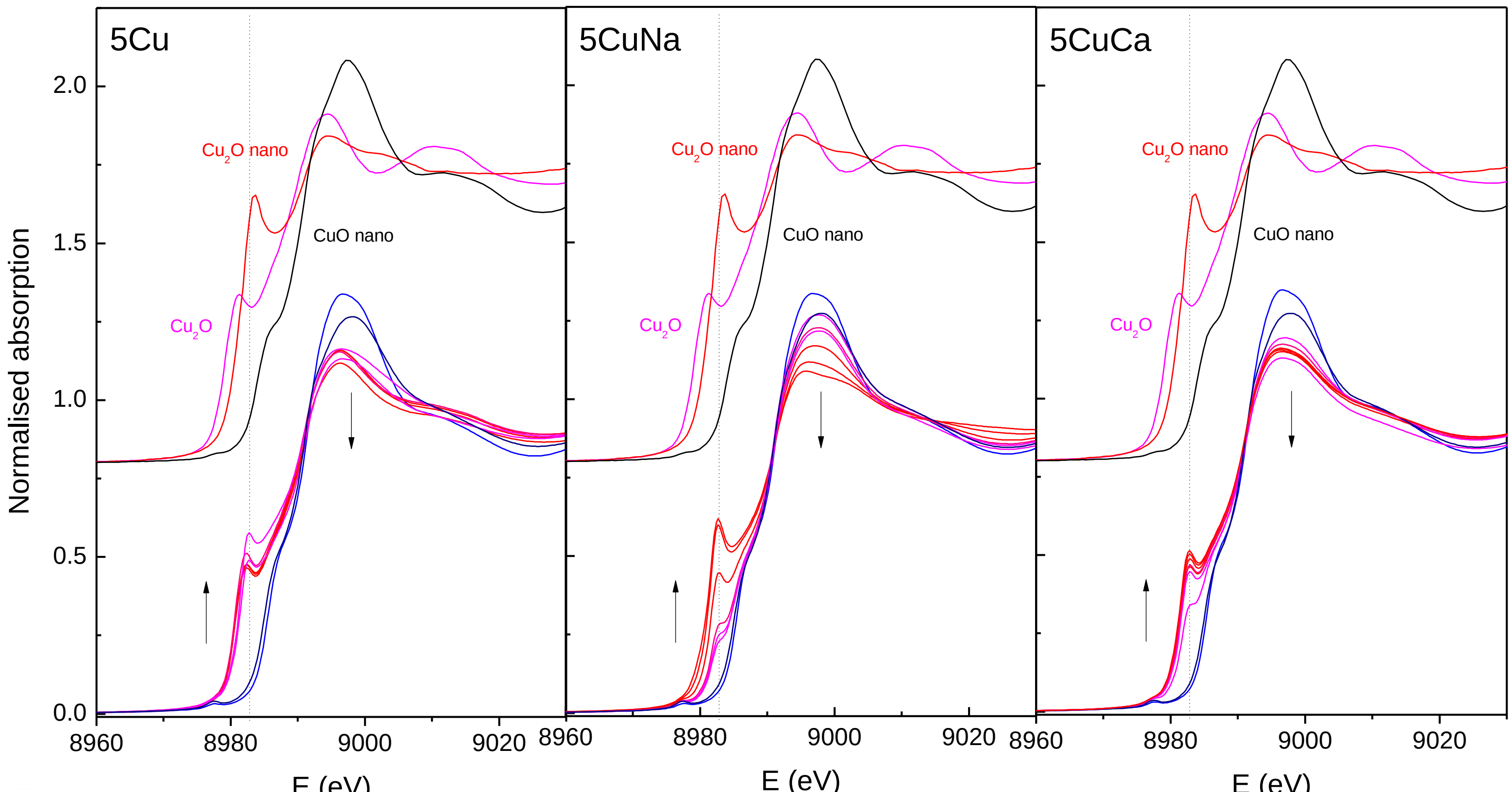
- 1630 cm^{-1} surface bound hydroxyls
- 1890 cm^{-1} trace nitrates
- 2130 cm^{-1} monoxide species
- 2339 cm^{-1} surface bound CO_2
- 3000-3650 cm^{-1} surface bound hydroxyls



In situ XAS

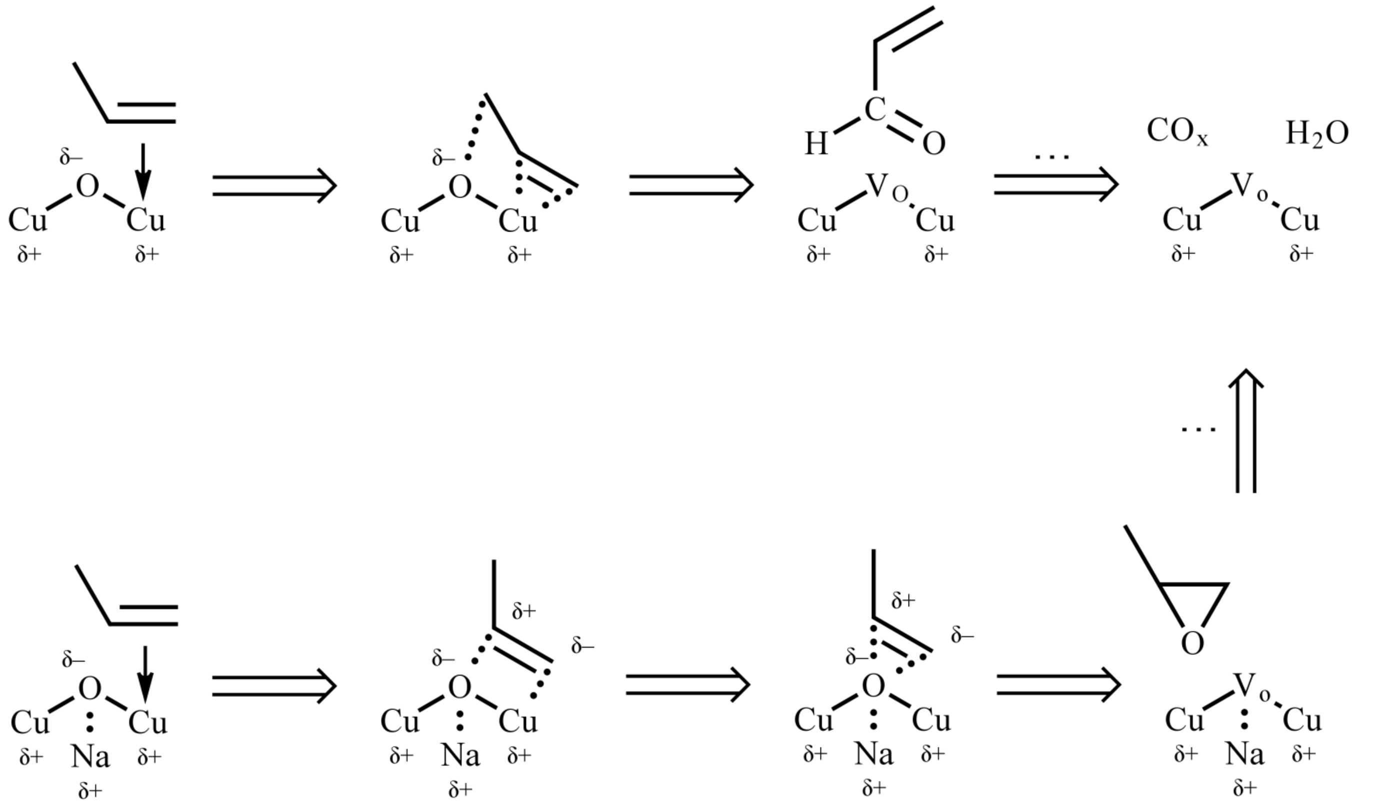

5Cu
5CuNa
5CuCa
Cu2O nano
CuO nano
Cu2O
Normalised absorption
2.0
1.5
1.0
0.5
0.0
8960
8980
9000
9020
8960
E (eV)
5Cu
5CuCa
5CuNa
Relative Cu+ content [%]
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
Time [min]

In situ XAS

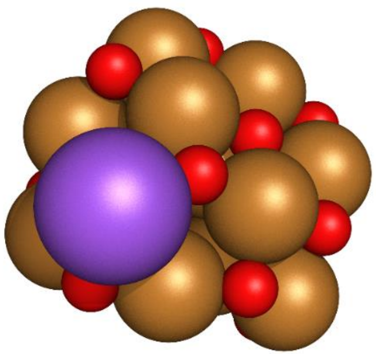


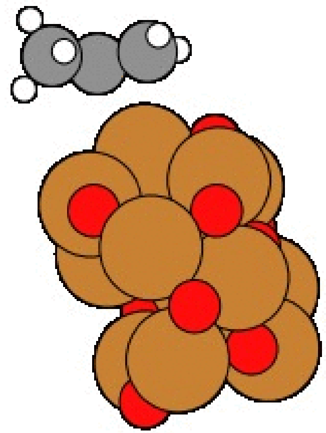
5Cu
5CuNa
5CuCa
Normalised absorption
2.0
1.5
1.0
0.5
0.0
Cu2O nano
CuO nano
Cu2O
8960
8980
9000
9020
E (eV)

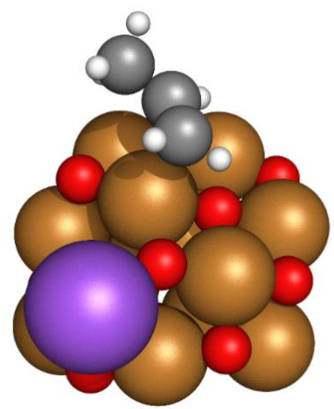
Tentative mechanism



Computational analysis

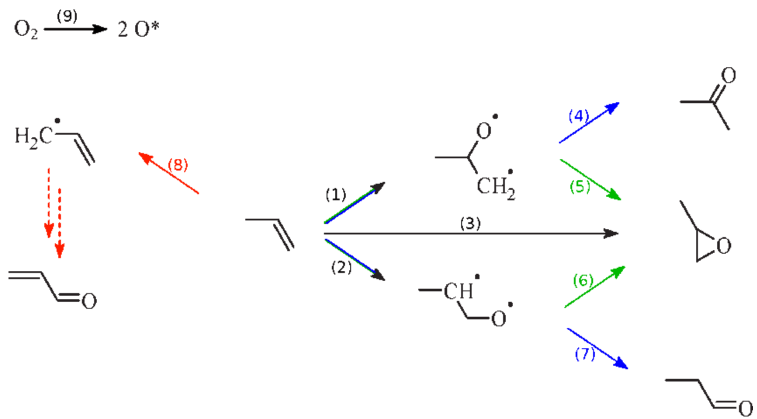


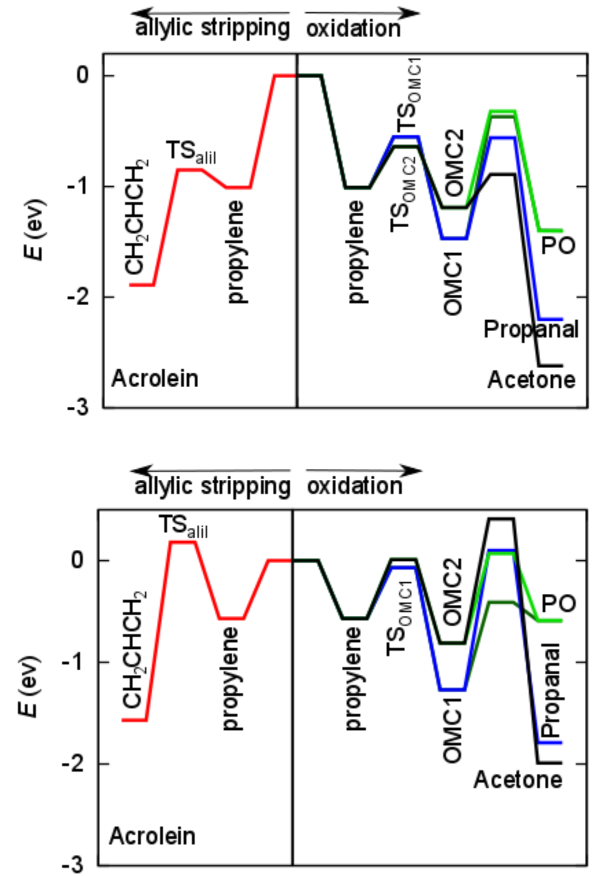




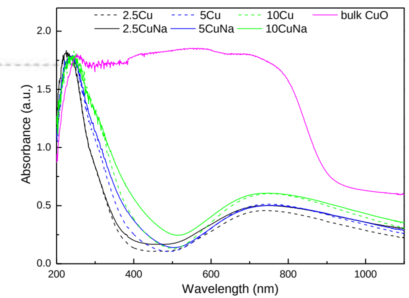
Sample	Cu-O bond distance measured, Å	Cu-O bond distance calculated, Å
5Cu	1.870	1.869
5CuNa	1.830	1.856
5CuCs	1.882	1.857
5CuCa	1.874	1.875

Computational analysis

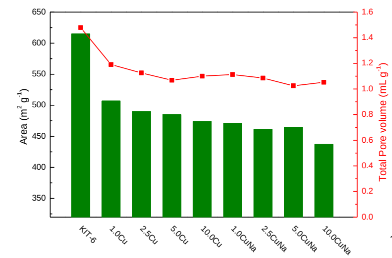




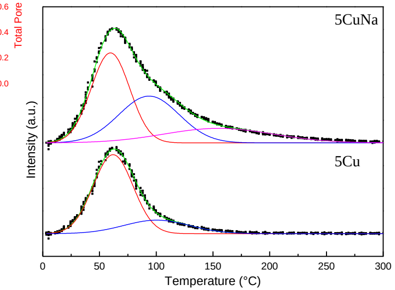
Conclusions



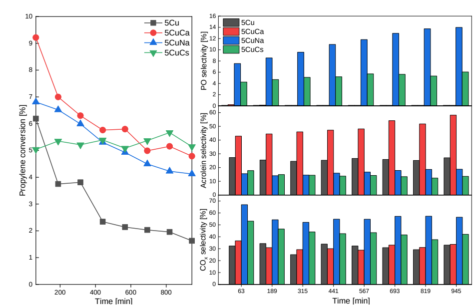
- The dilution hydrolysis technique produces promising selective and stable copper containing alkali modified catalysts



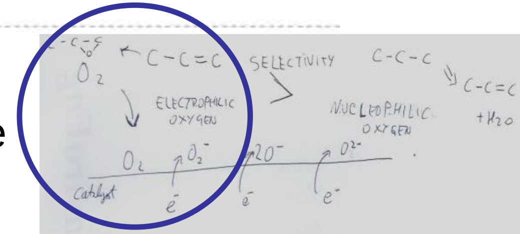
- Loading of copper into the pores of KIT-6 does not affect mesoporous ordering



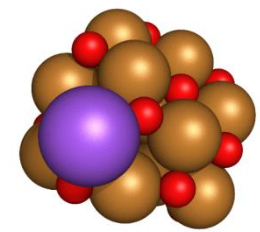
- Alkali addition generates additional basic sites on the catalyst surface
- The intermediate basic sites are selective for propylene epoxidation



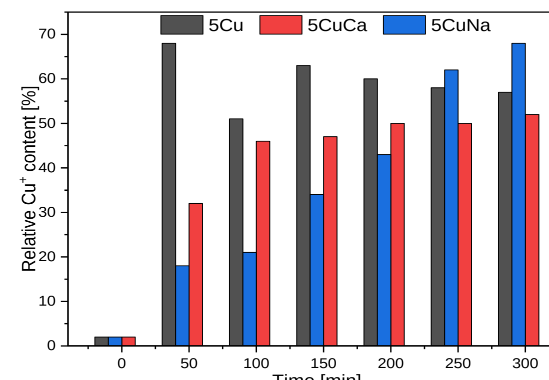
Conclusions



- Alkali addition reduces the nucleophilic properties of the active oxygen species and significantly increases catalyst stability



- It increases oxygen binding strength, which reduces bond length
- Earth alkali modification has the reverse effect
- The amount of copper (I) is not the (only) determining factor for PO selectivity



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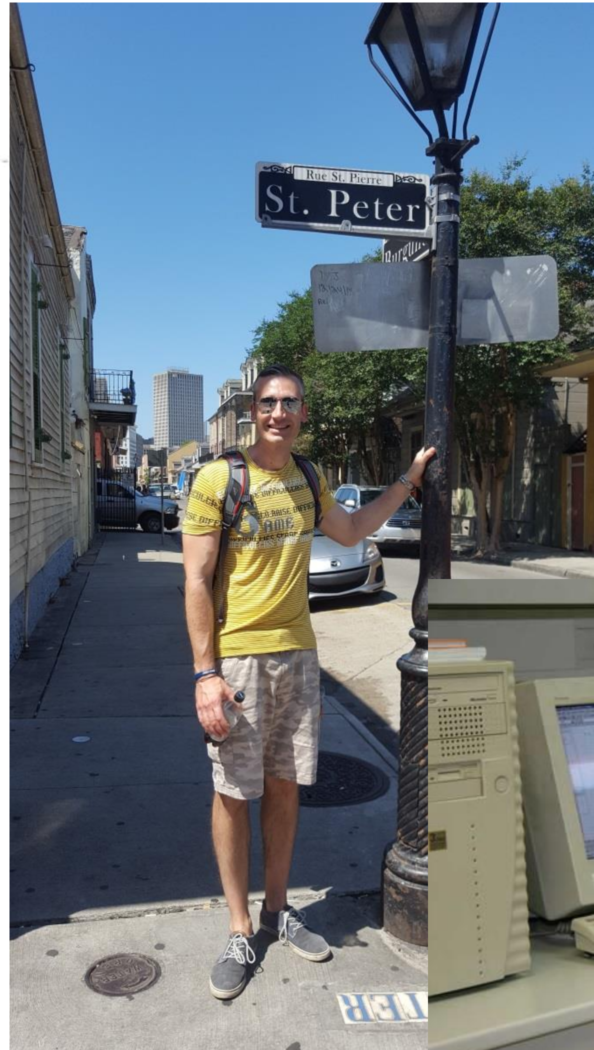

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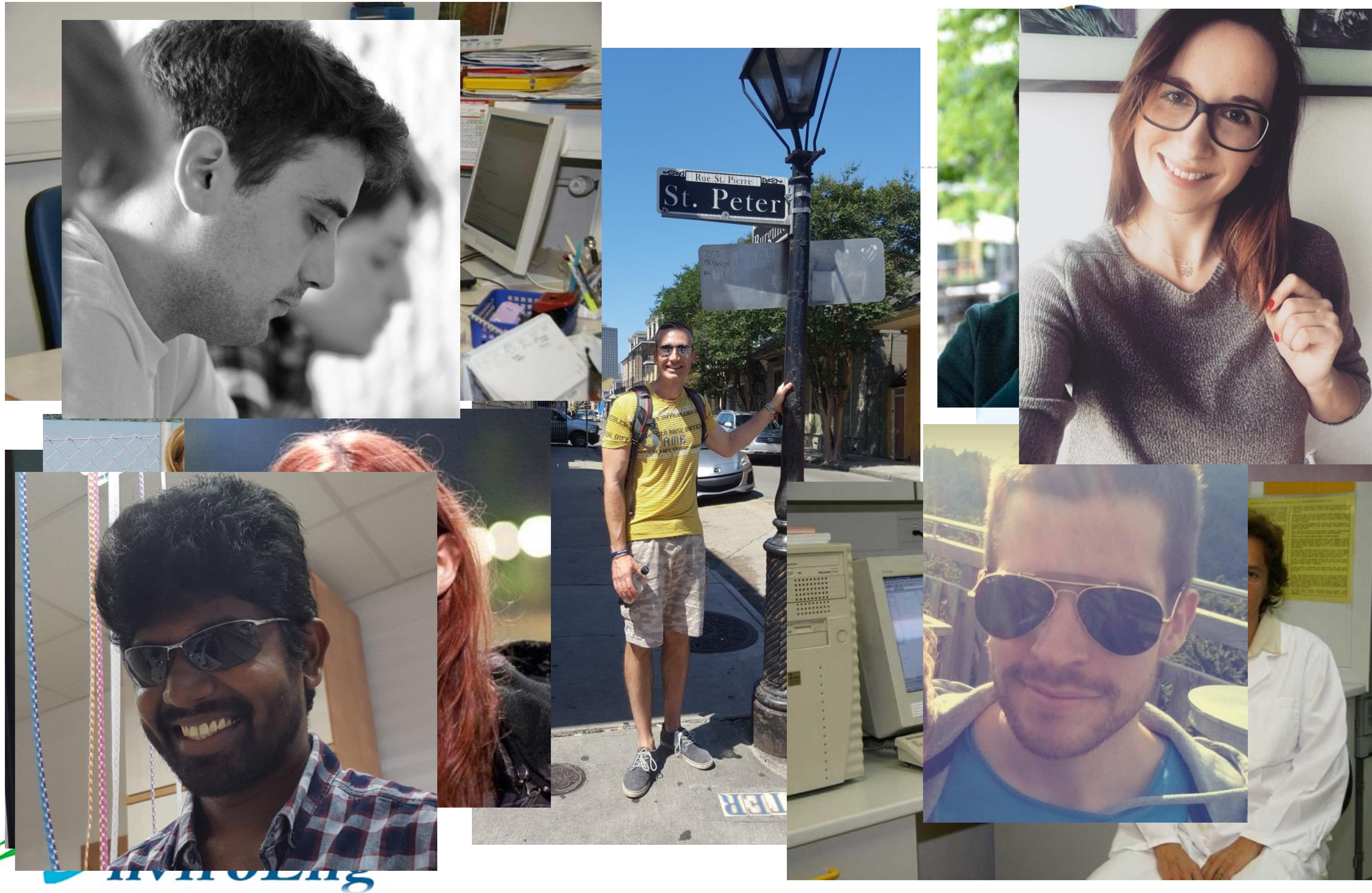
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St. Peter

Thank you!