XIV School on Synchrotron Radiation:
Fundamentals, Methods and Applications
Muggia, Italy / 18-29 September 2017

SILS
SOCIETA' ITALIANA DI LUCE DI SINCROTRONE

Elettra Sincrotrone Trieste

Catalysis with SR: ex-situ, in –situ and Operando conditions

C. Lamberti
Department of Chemistry, University of Turin (Italy)
Souther Federal University Rostov-on-Don, Russia

Nanostructured Interfaces and Surfaces
Centre of Excellence

Università di Torino

A selection of several other examples:

CHEMICAL REVIEWS

Review

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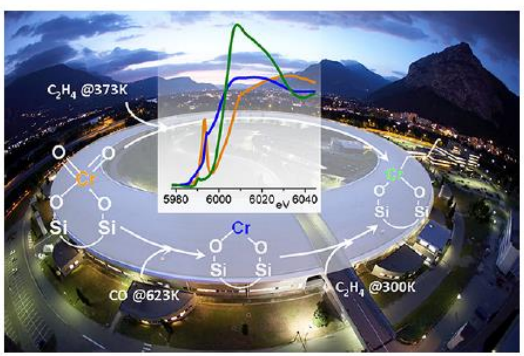
Reactivity of Surface Species in Heterogeneous Catalysts Probed by In Situ X-ray Absorption Techniques

Silvia Bordiga,[†] Elena Groppo,[†] Giovanni Agostini,[†] Jeroen A. van Bokhoven,[‡,§] and Carlo Lamberti*[,†]

[†]Department of Chemistry and NIS Centre of Excellence, Università di Torino and INSTM Reference Center, Via P. Giuria 7, 10125 Torino, Italy

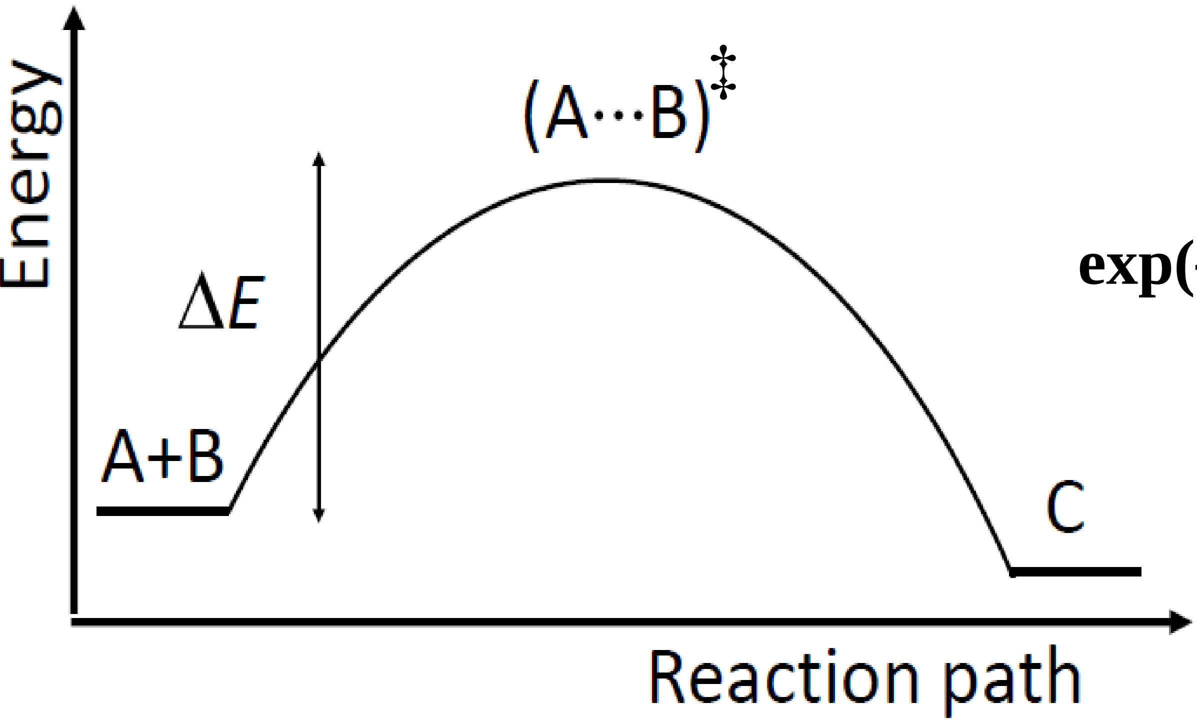
[‡]ETH Zurich, Institute for Chemical and Bioengineering, HCI E127 8093 Zurich, Switzerland

[§]Laboratory for Catalysis and Sustainable Chemistry (LSK) Swiss Light Source, Paul Scherrer Instituteaul Scherrer Institute, Villigen, Switzerland



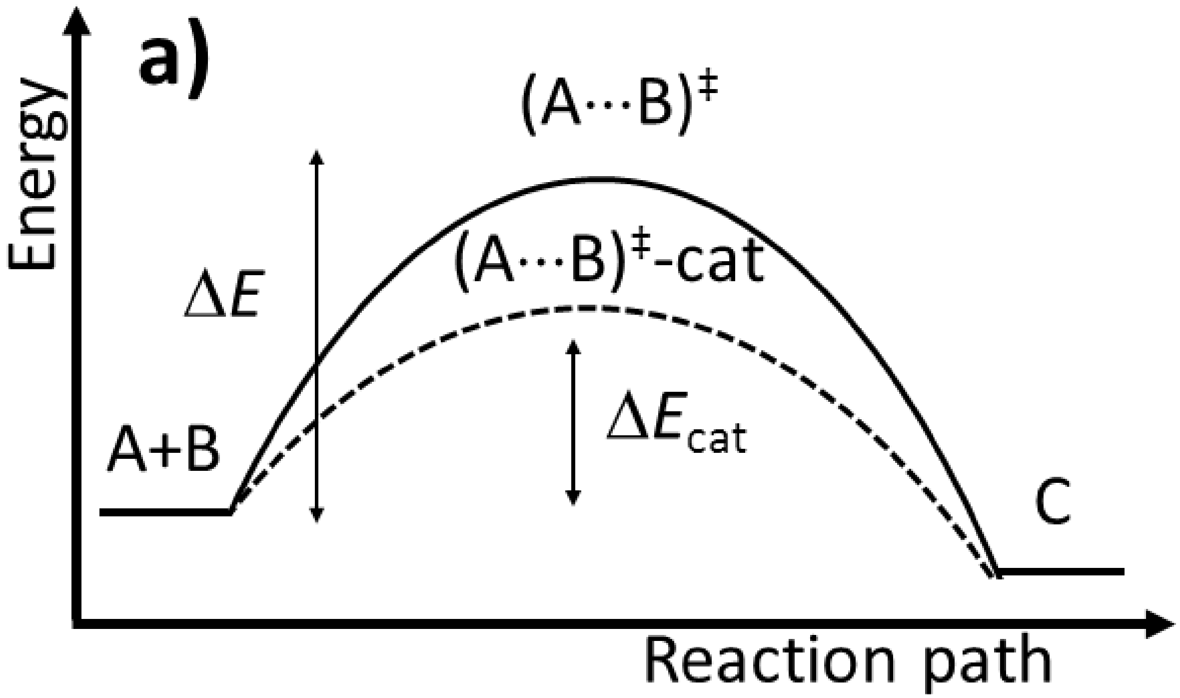
Chem. Rev., **113** (2013) 1736–1850

What does a catalyst do?

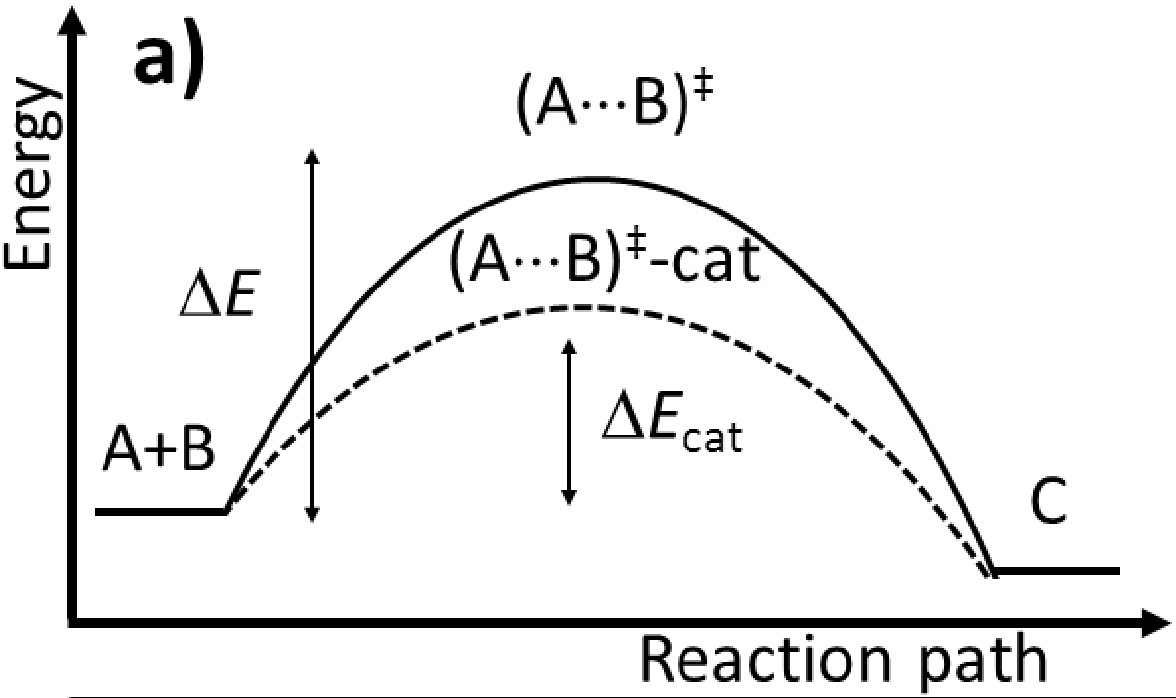


$\exp(-\Delta E/k_B T)$

What does a catalyst do?

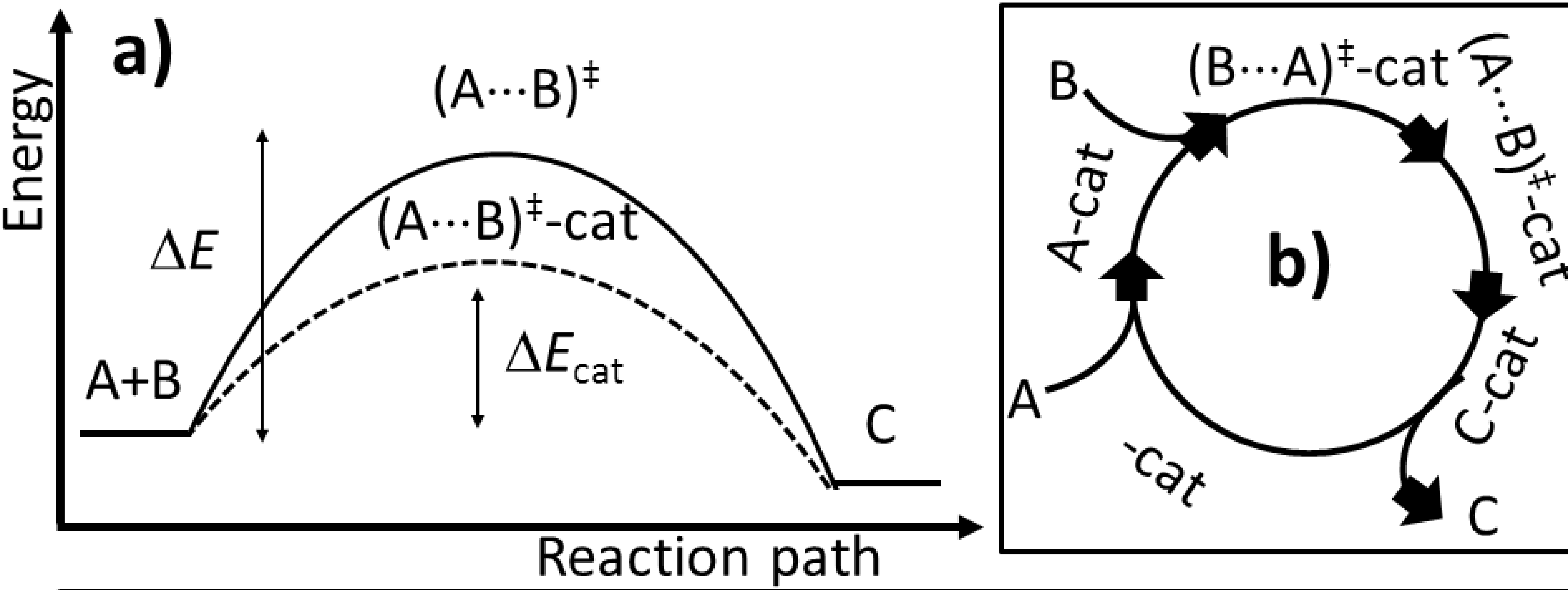


What does a catalyst do?



c)	A+B $\rightleftharpoons$ x% C + y% D + (100 − x − y)% E	A+B $\overset{cat}{\rightleftharpoons}$ ~100% C

What does a catalyst do?

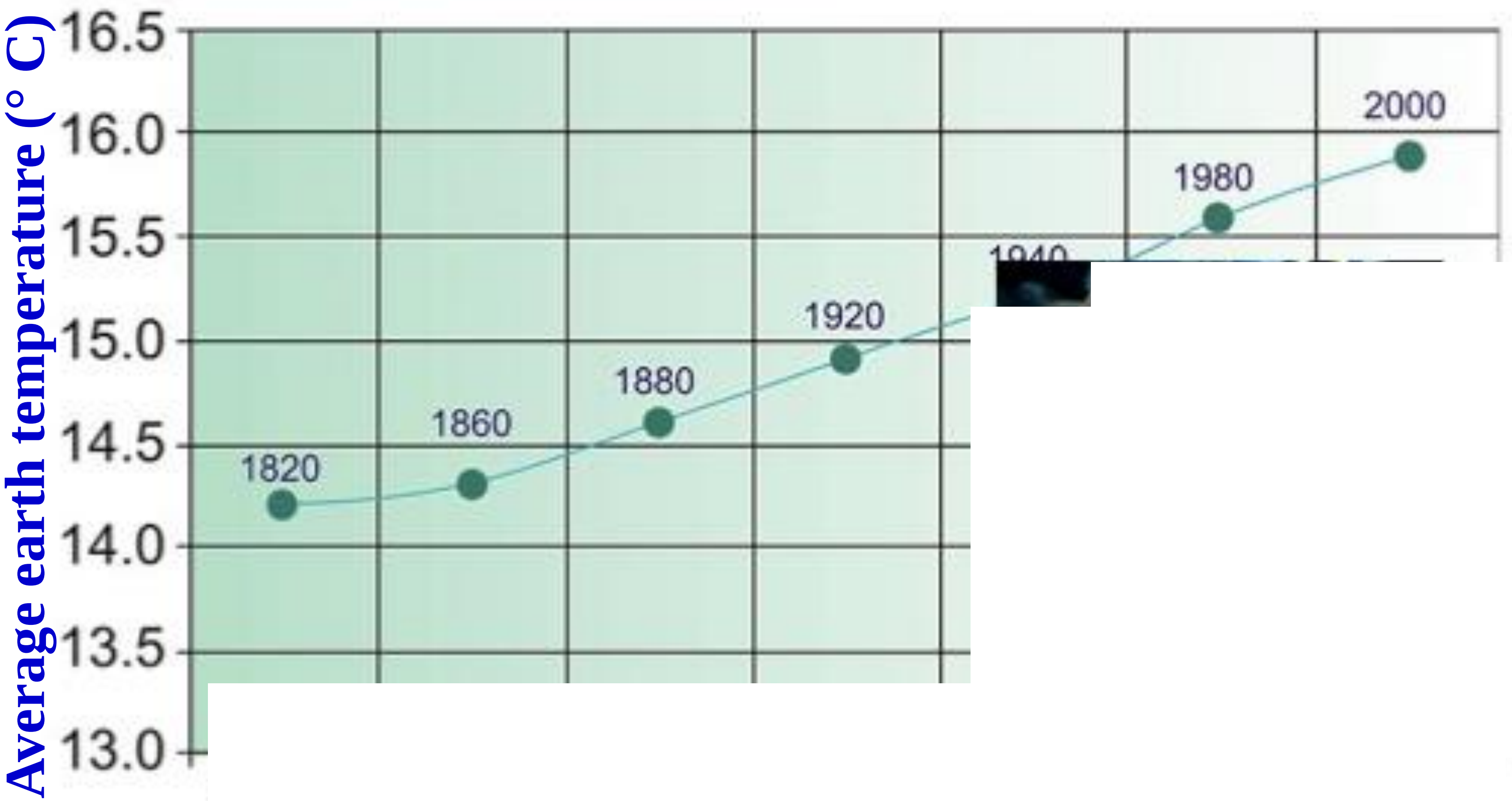


c) $A+B \rightleftharpoons x\%\ C + y\%\ D + (100 - x - y)\%\ E$ | $A+B \overset{cat}{\rightleftharpoons} \sim 100\%\ C$

The complexity of a catalyst:

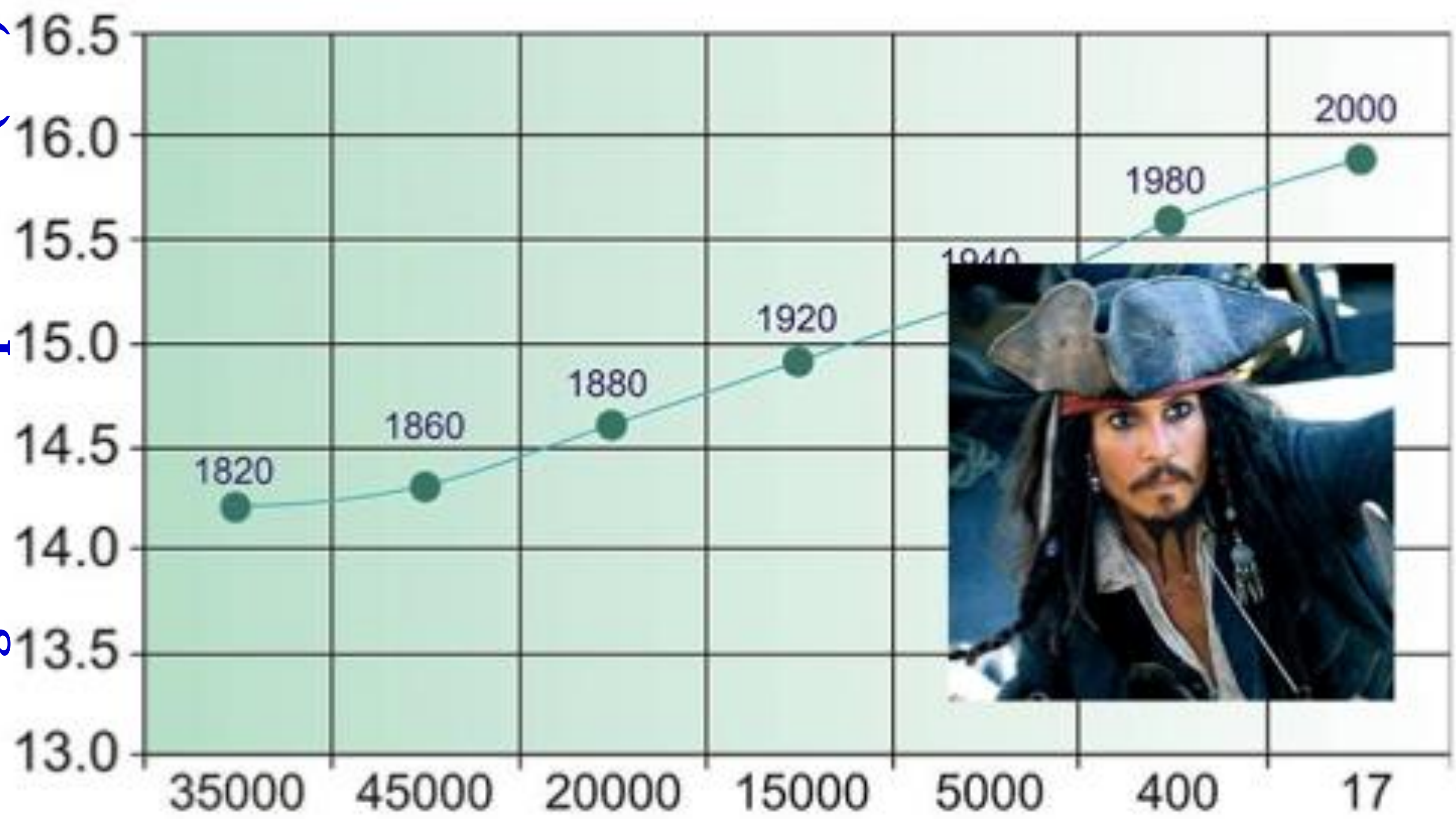
Nature of the support
Concentration of the active phase
Deposition methods
Addition of dopants
P, T
Possible presence of spectators
Aging effects
Poisoning
Deactivation

New researchs discover the actual cause of the global warming

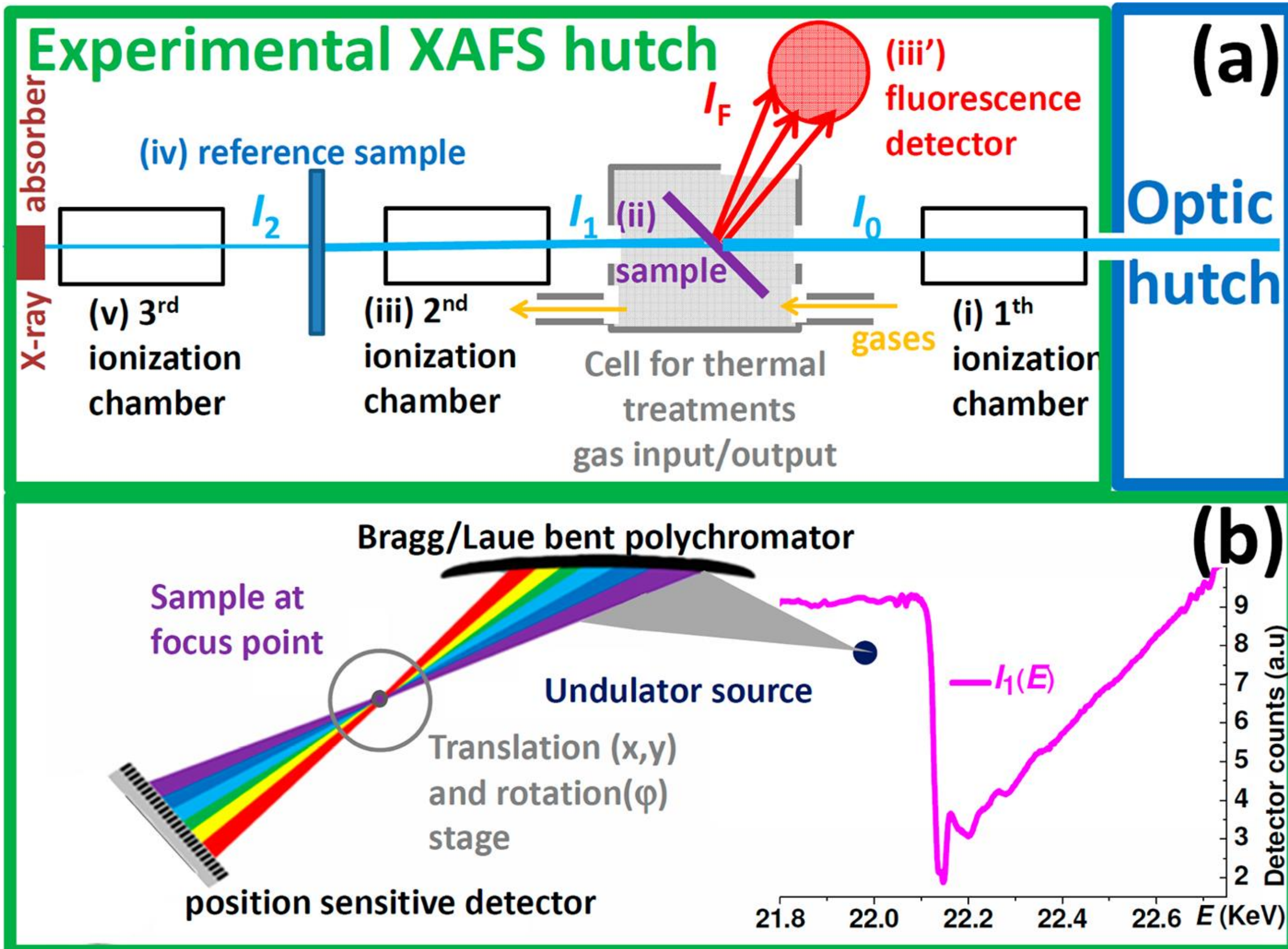


New researchs discover the actual cause of the global warming

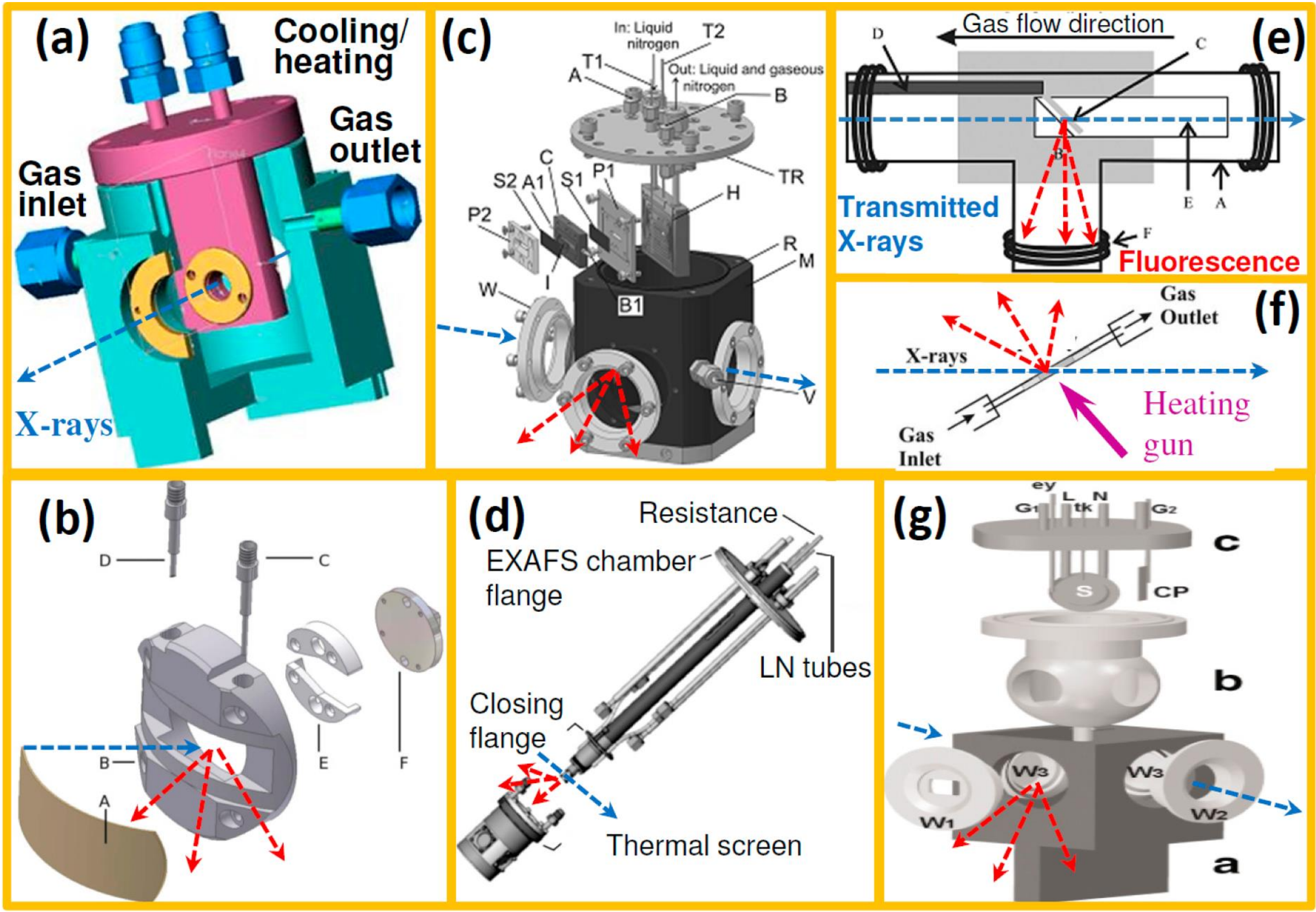
Average earth temperature (° C)



Number of Pirats actives in the caribbean sea

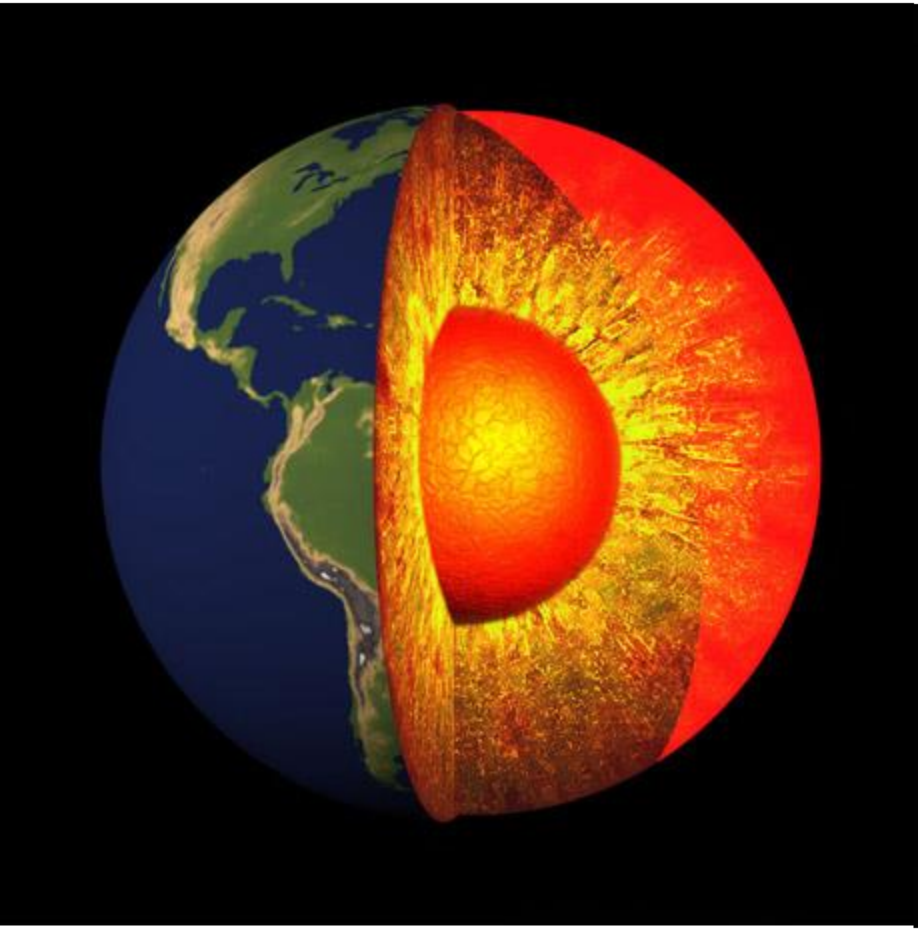


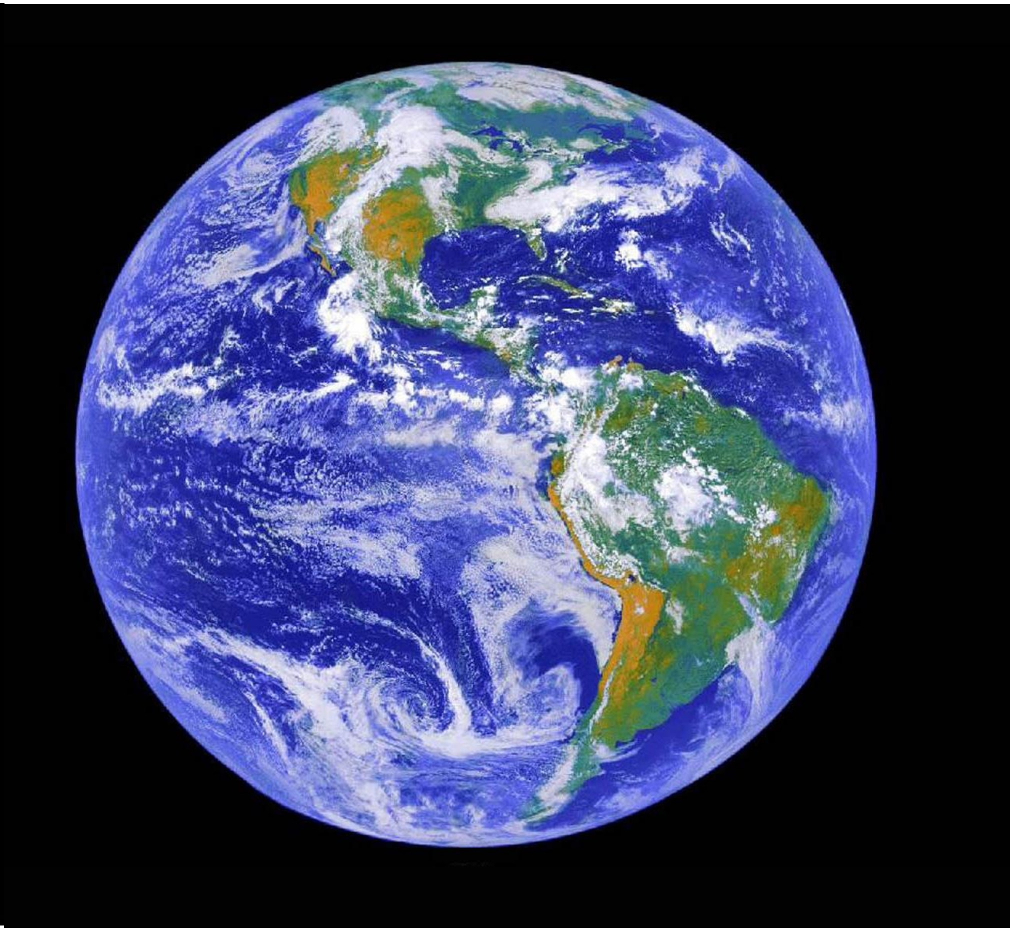
Bordiga et al. *Chem. Rev.*, **113** (2013) 1736–1850



Bordiga et al. *Chem. Rev.*, **113** (2013) 1736–1850

The relevance of surfaces



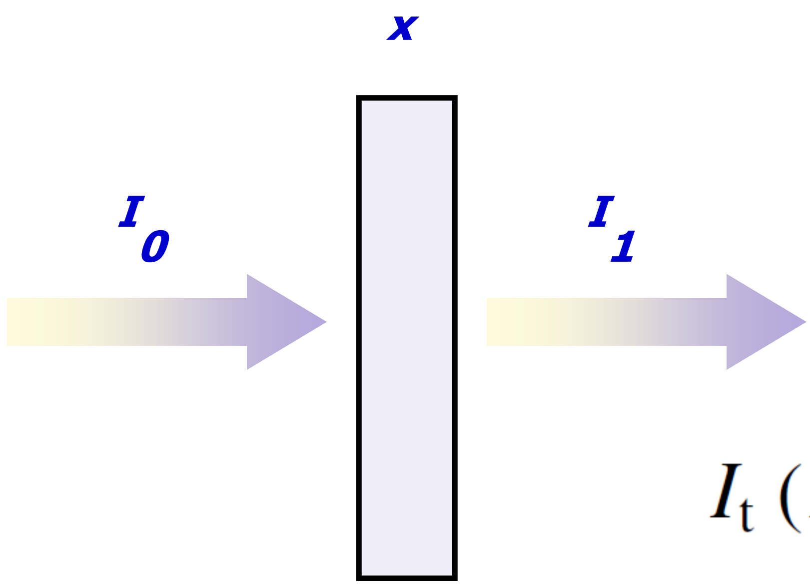


There is NO life on earth !

NO, it is a surface phenomenon !

We avoided an invasion because aliens had no surface sensitive techniques

Transmission techniques are basically bulk techniques



Transmission geometry

IR
hard XAS
XRPD

$$I_t(E) = I_0(E)\,e^{-\mu(E)x}$$

$$\mu(E)\,x = -\ln\left(\frac{I_t}{I_0}\right) = \ln\left(\frac{I_0}{I_t}\right)$$

... but catalysis is related with surface sites

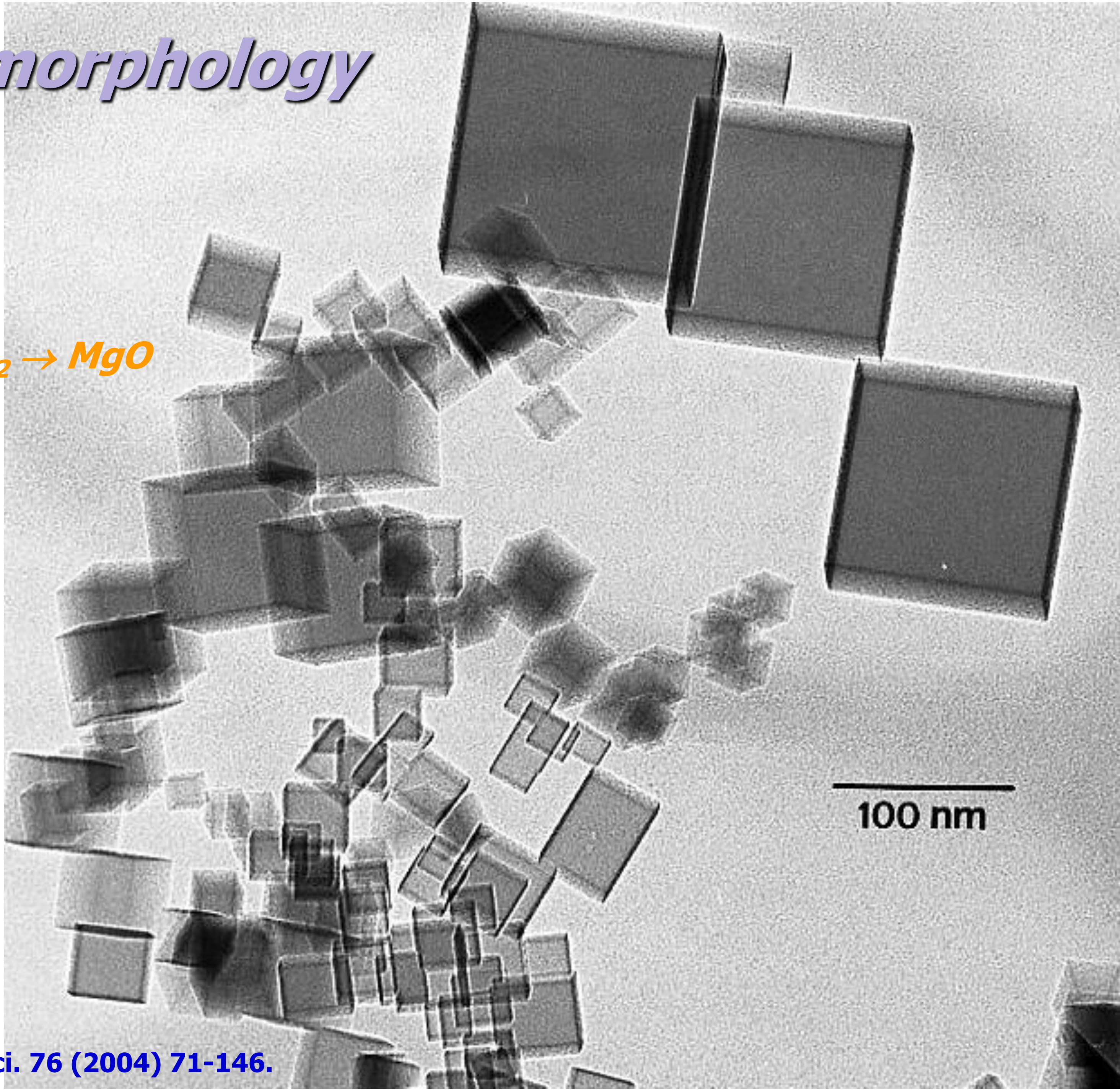
XPS; UPS; soft-XAS; hard XAS detected in EY

MgO morphology

MgO smoke

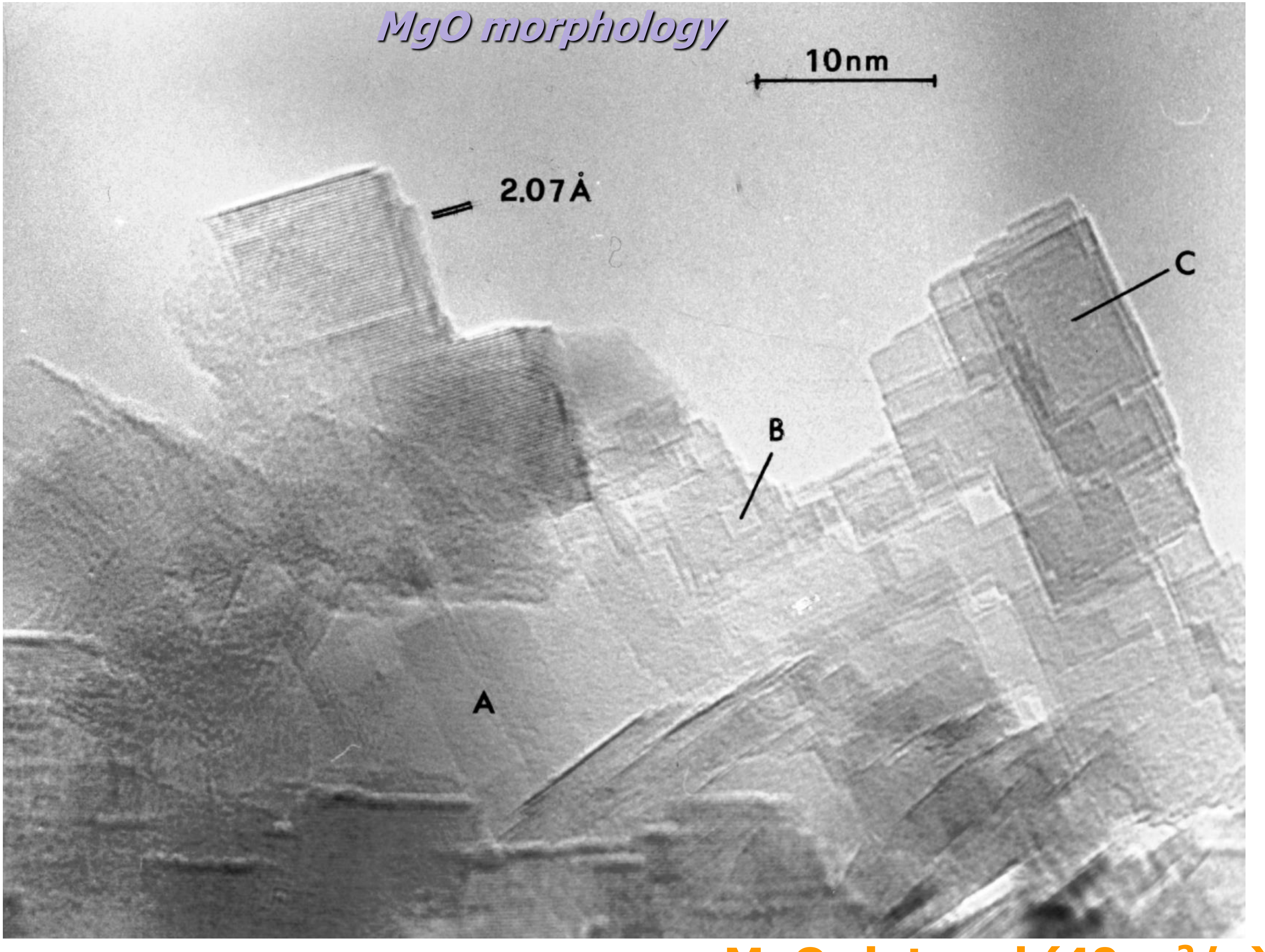
$Mg(metal) + \frac{1}{2} O_2 \rightarrow MgO$

(< 1 m^2/g)



Spoto et al. Prog. Surf. Sci. 76 (2004) 71-146.

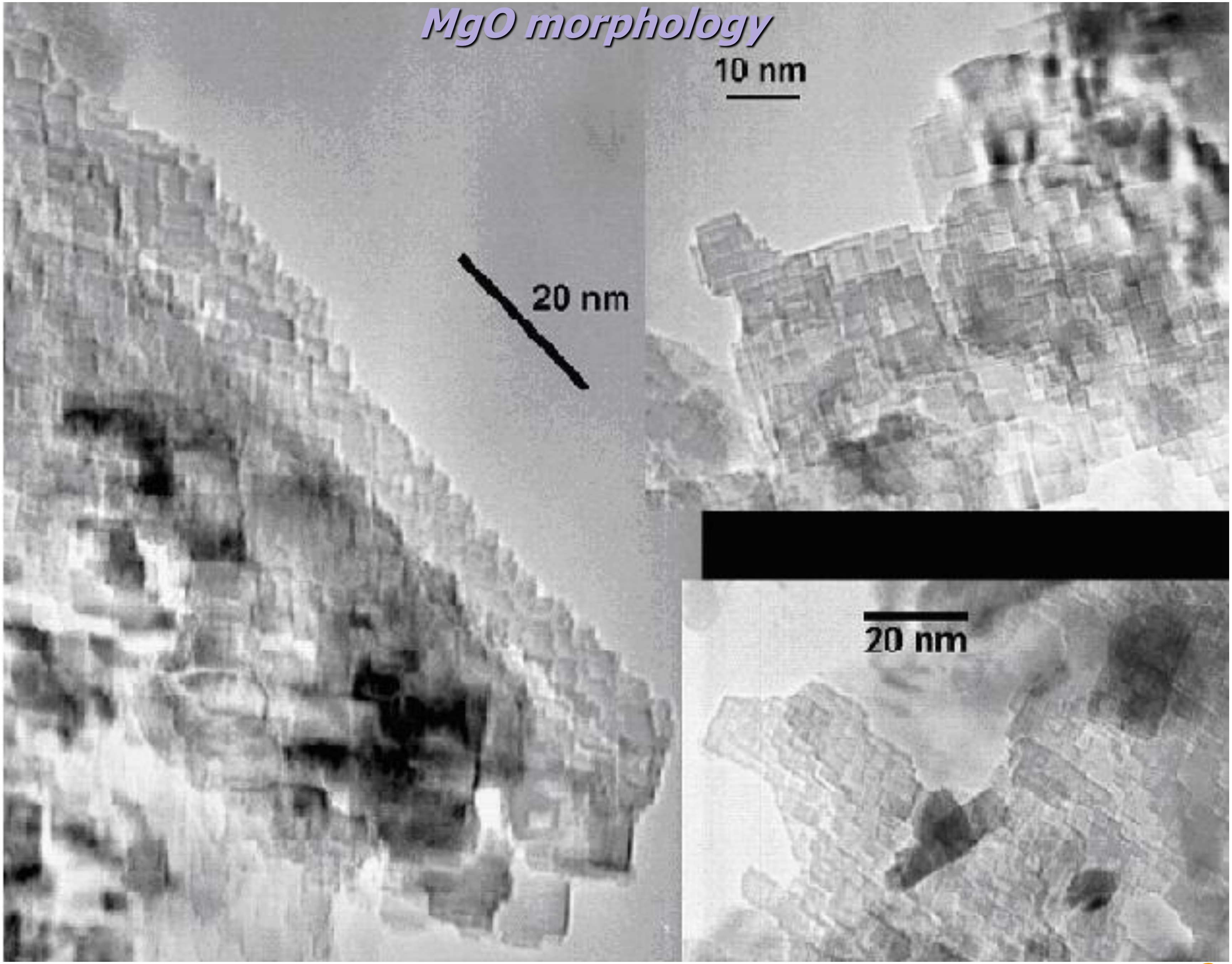
MgO morphology



MgO sintered (40 m^2/g)

Spoto et al. Prog. Surf. Sci. 76 (2004) 71-146.

MgO morphology



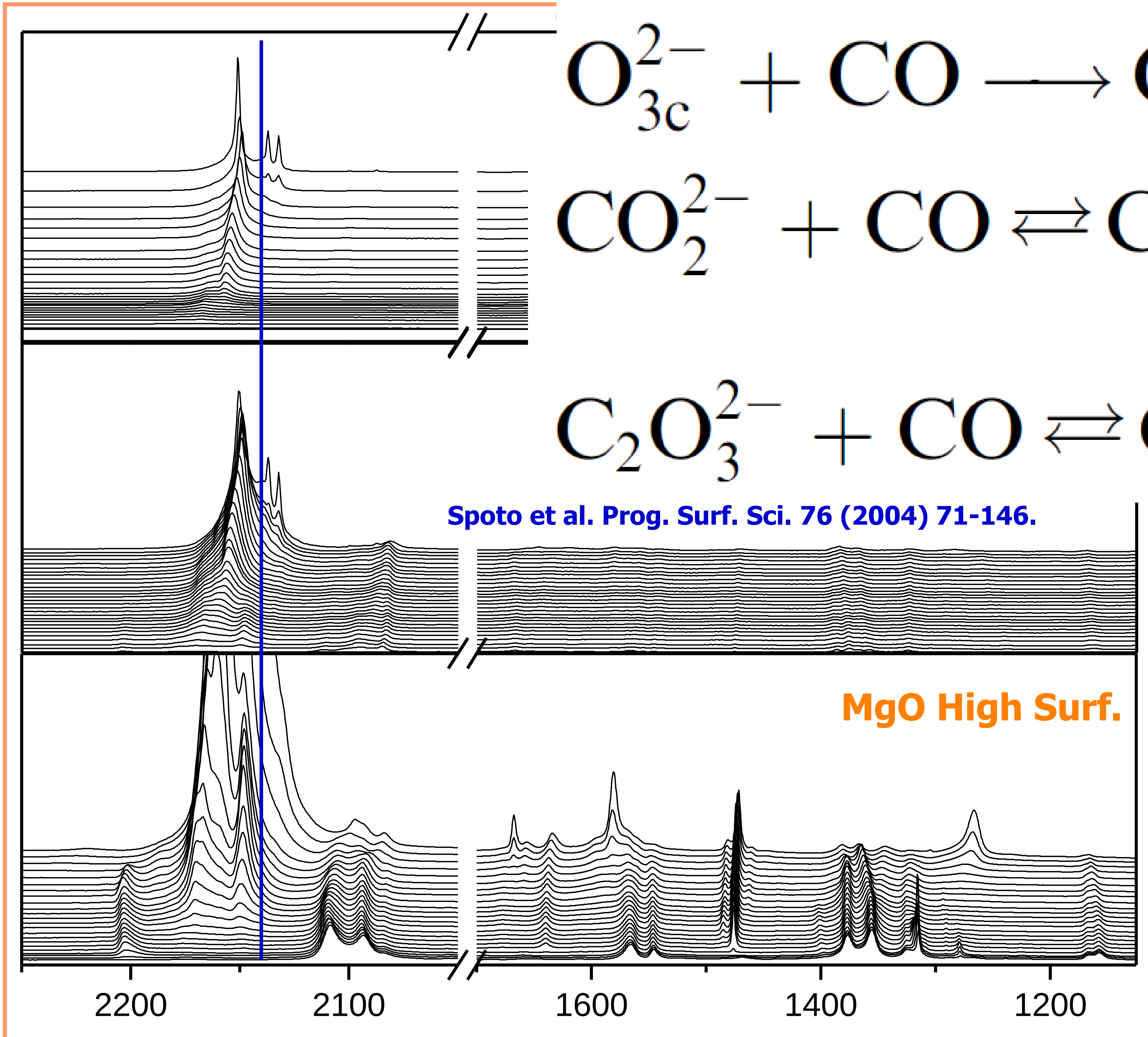
Spoto et al. Prog. Surf. Sci. 76 (2004) 71-146.

MgO sintered (230 m^2/g)

$$O_{3c}^{2-} + CO \longrightarrow CO_2^{2-}$$

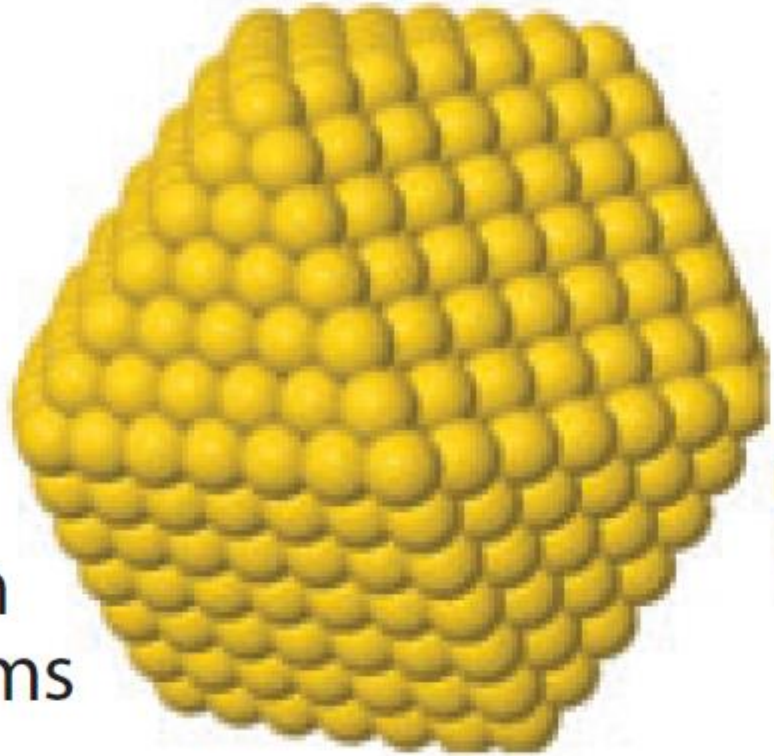
$$CO_2^{2-} + CO \rightleftarrows C_2O_3^{2-}$$

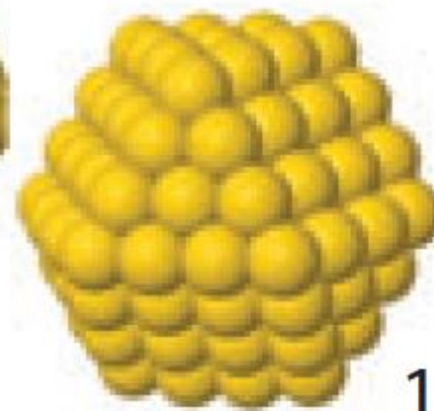
$$C_2O_3^{2-} + CO \rightleftarrows C_3O_4^{2-}$$



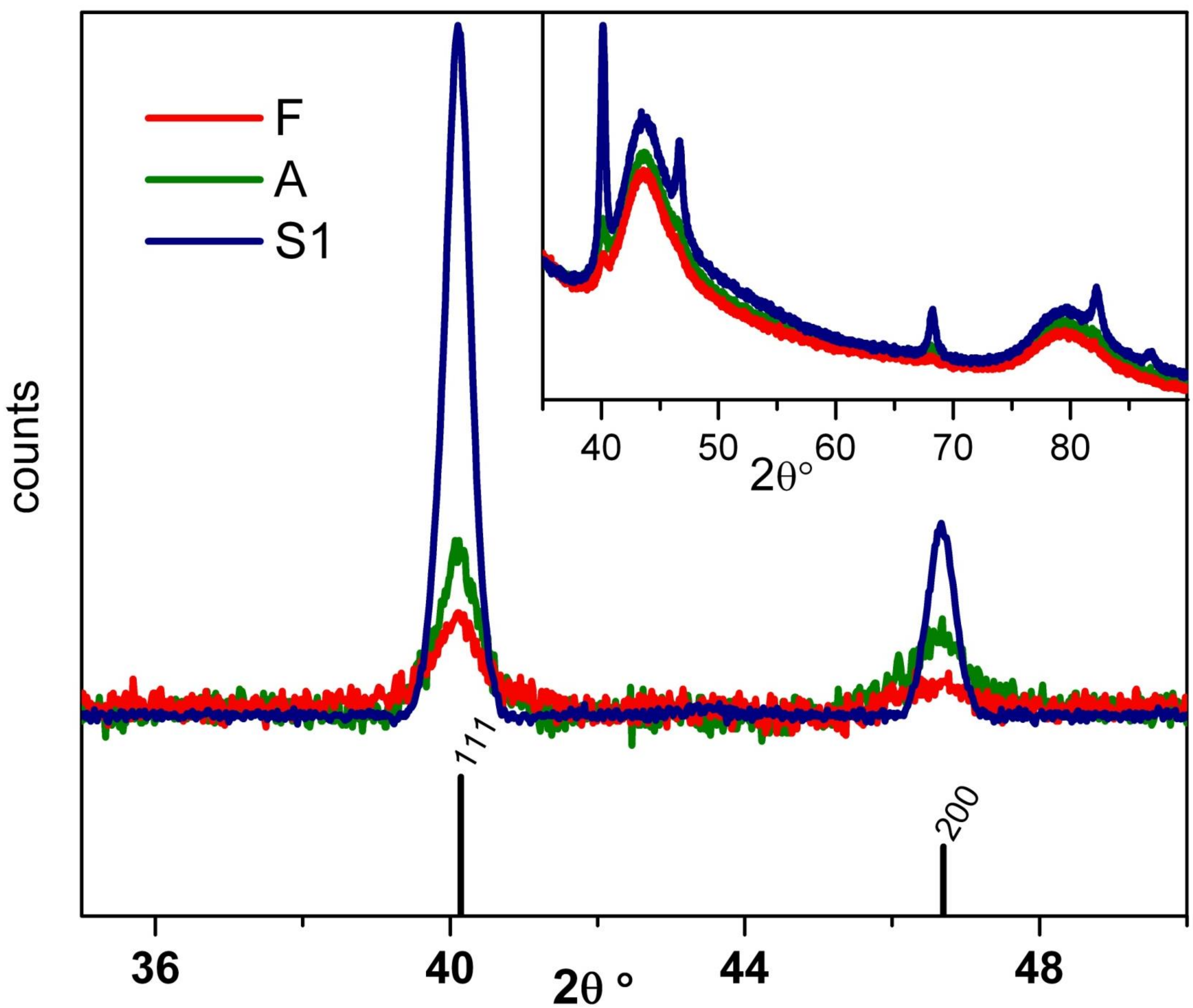
Spoto et al. Prog. Surf. Sci. 76 (2004) 71-146.

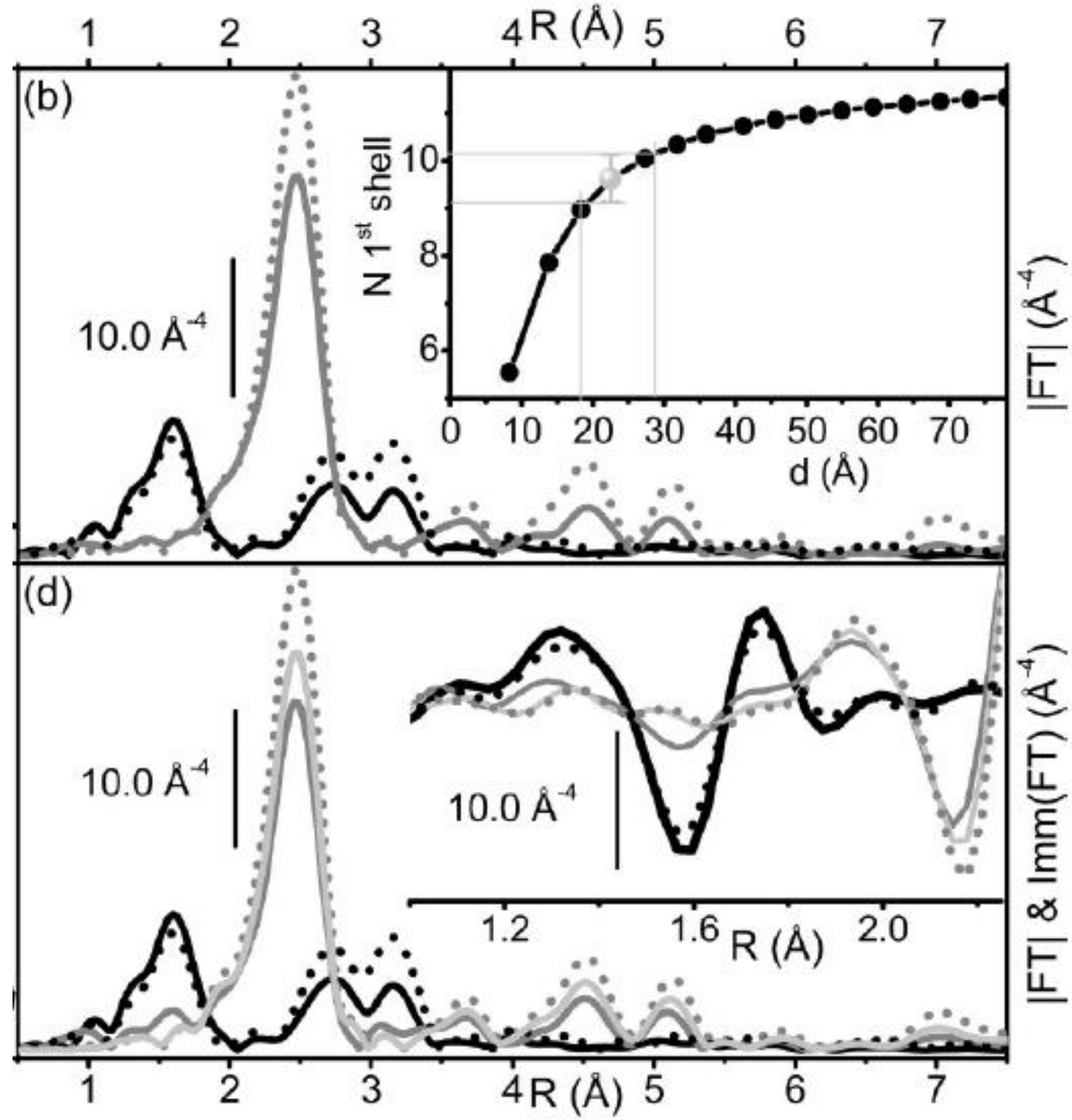
3.4 nm
923 atoms





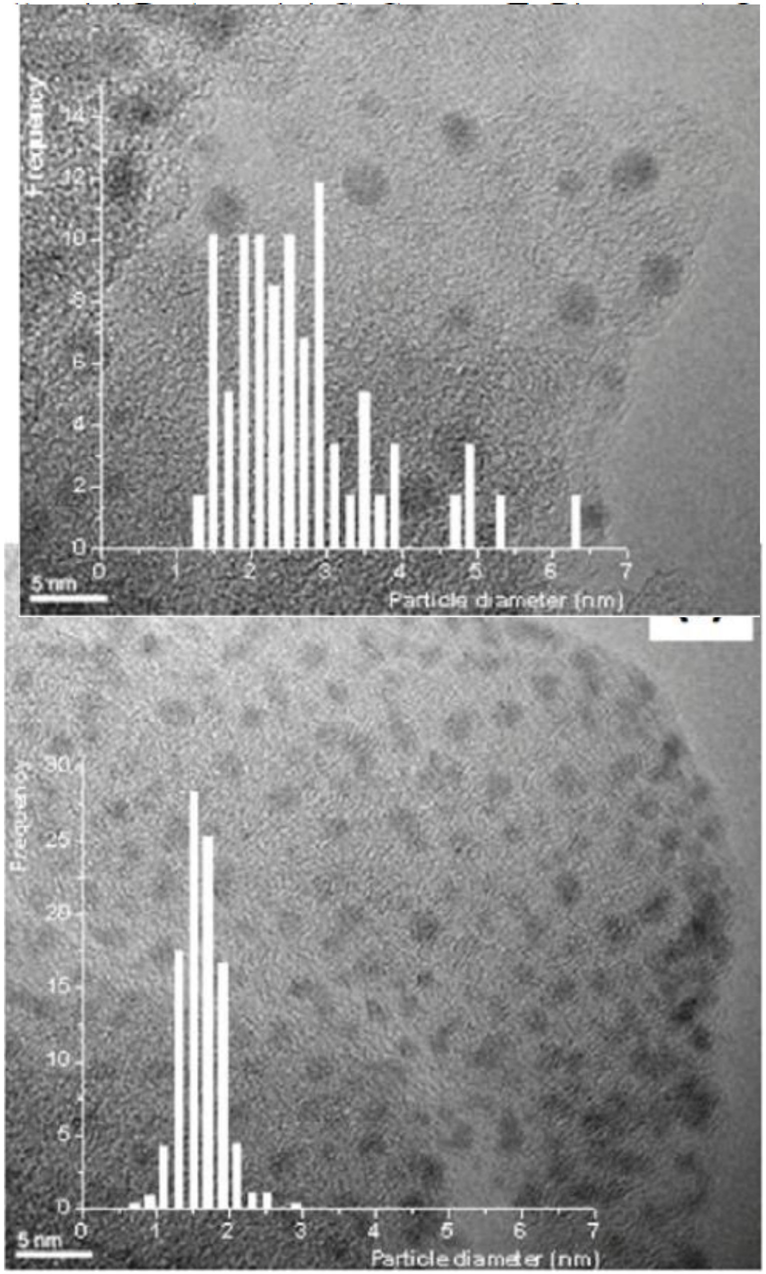
1.7 nm
147 atoms

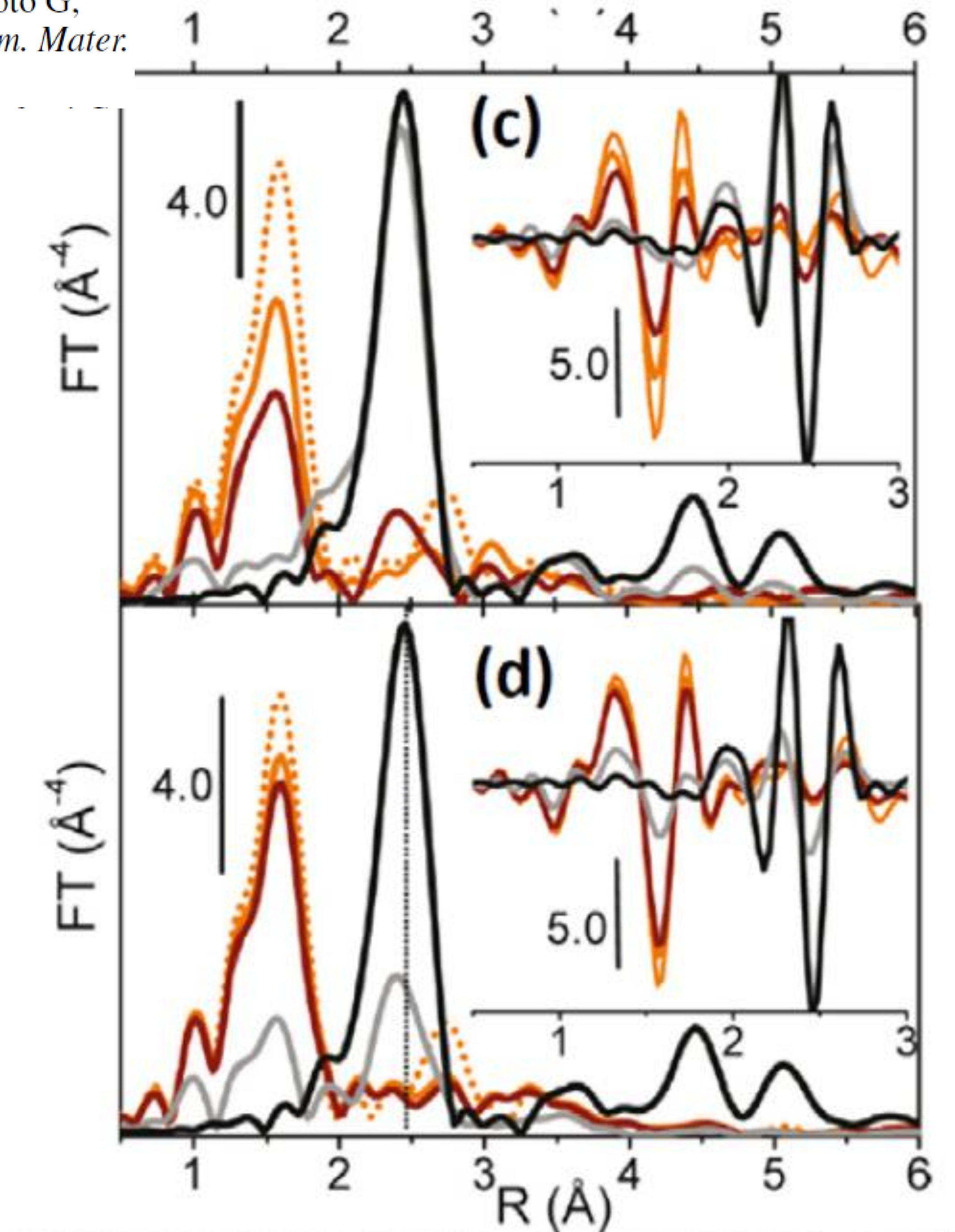

F
A
S1
counts
111
200
36
40
44
48
2θ °
40
50
60
70
80
2θ°

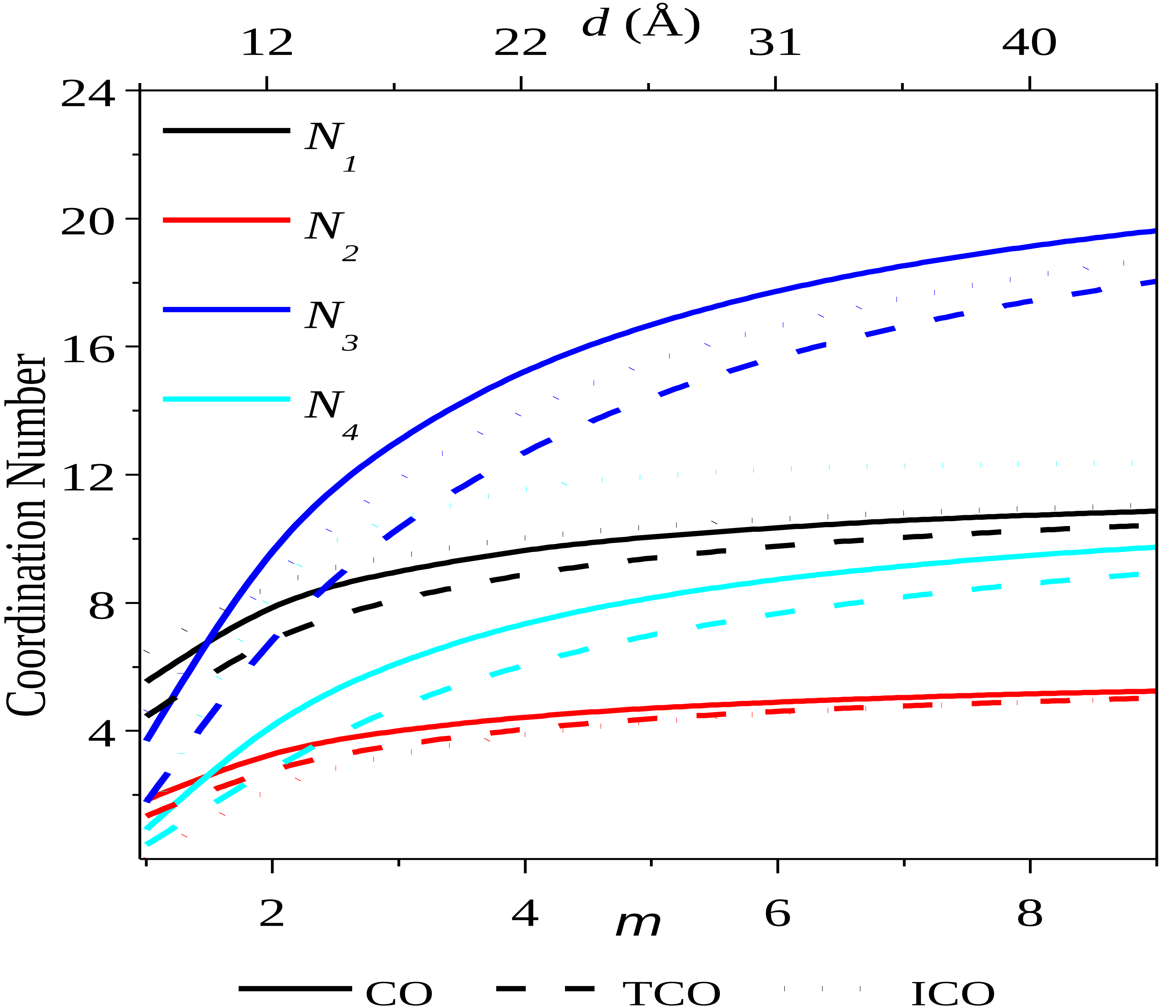


R (Å)
(b)
10.0 Å^{-4}
N 1st shell
d (Å)
|FT| (Å^{-4})
(d)
10.0 Å^{-4}
10.0 Å^{-4}
R (Å)
|FT| & Imm(FT) (Å^{-4})
R (Å)

Groppo E, Liu W, Zavorotynska O, Agostini G, Spoto G, Bordiga S, Lamberti C and Zecchina A 2010 *Chem. Mater.* **22** 2297







Frenkel, et al. J. Phys. Chem. B 2001, 105, 12689

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AUGUST 24, 2017
VOLUME 121
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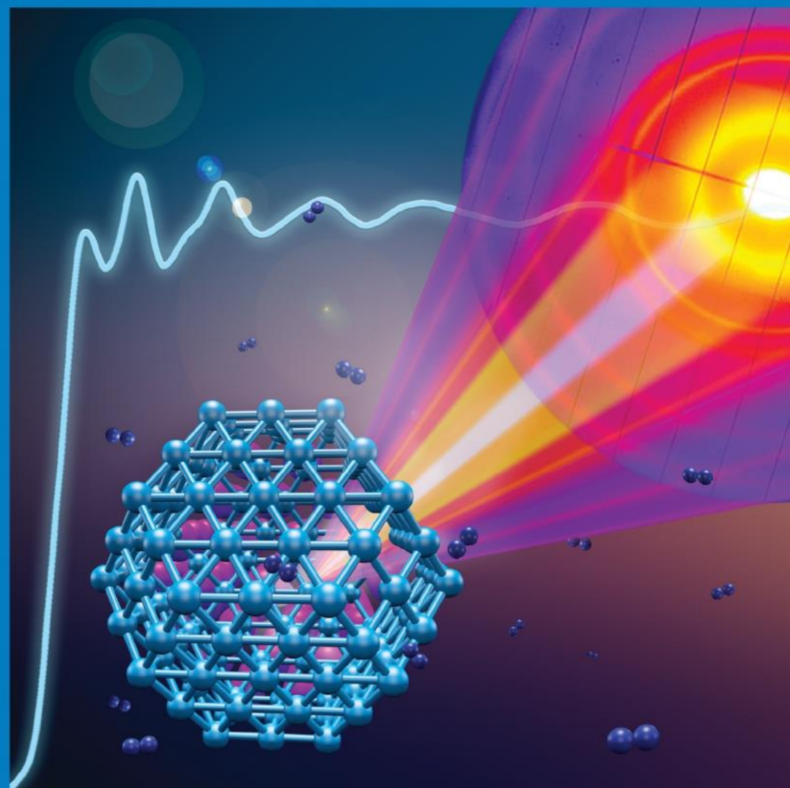
THE JOURNAL OF PHYSICAL CHEMISTRY C



Core–Shell Structure of Palladium Hydride Nanoparticles Revealed by X-ray Absorption Spectroscopy and Diffraction

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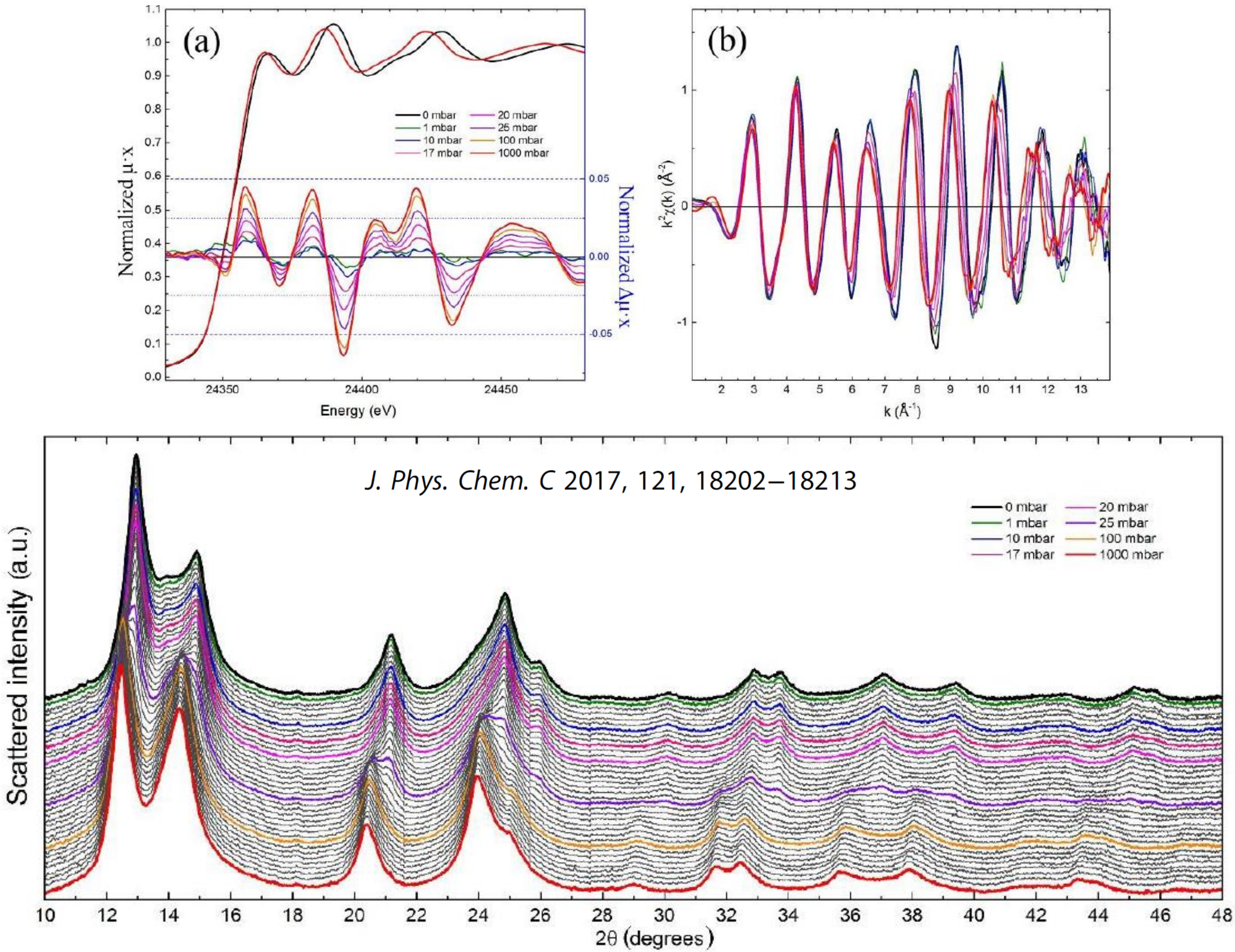
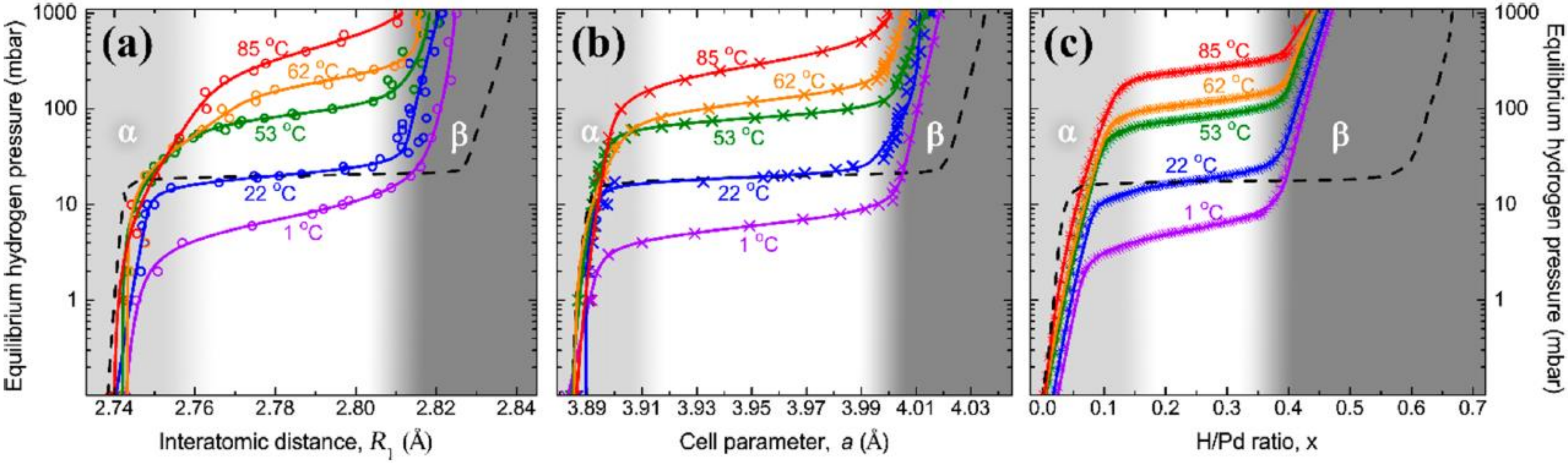
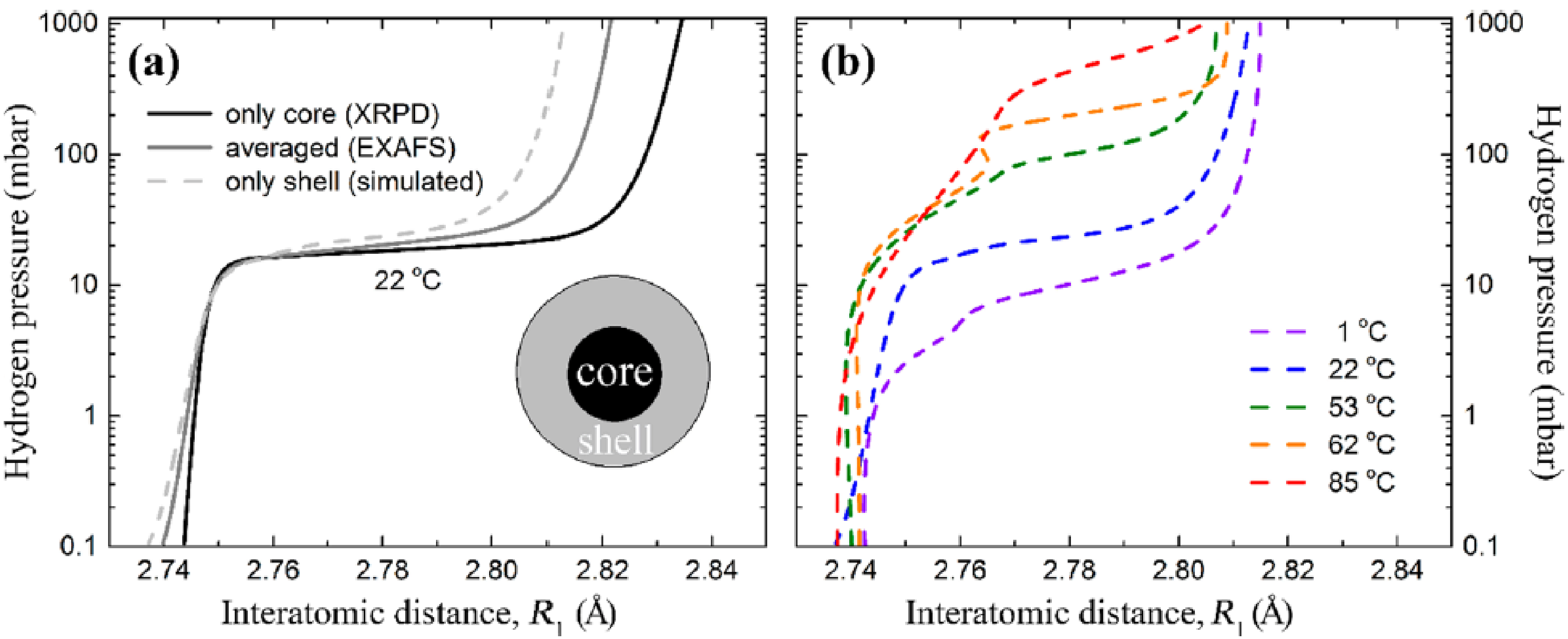
J. Phys. Chem. C 2017, 121, 18202−18213

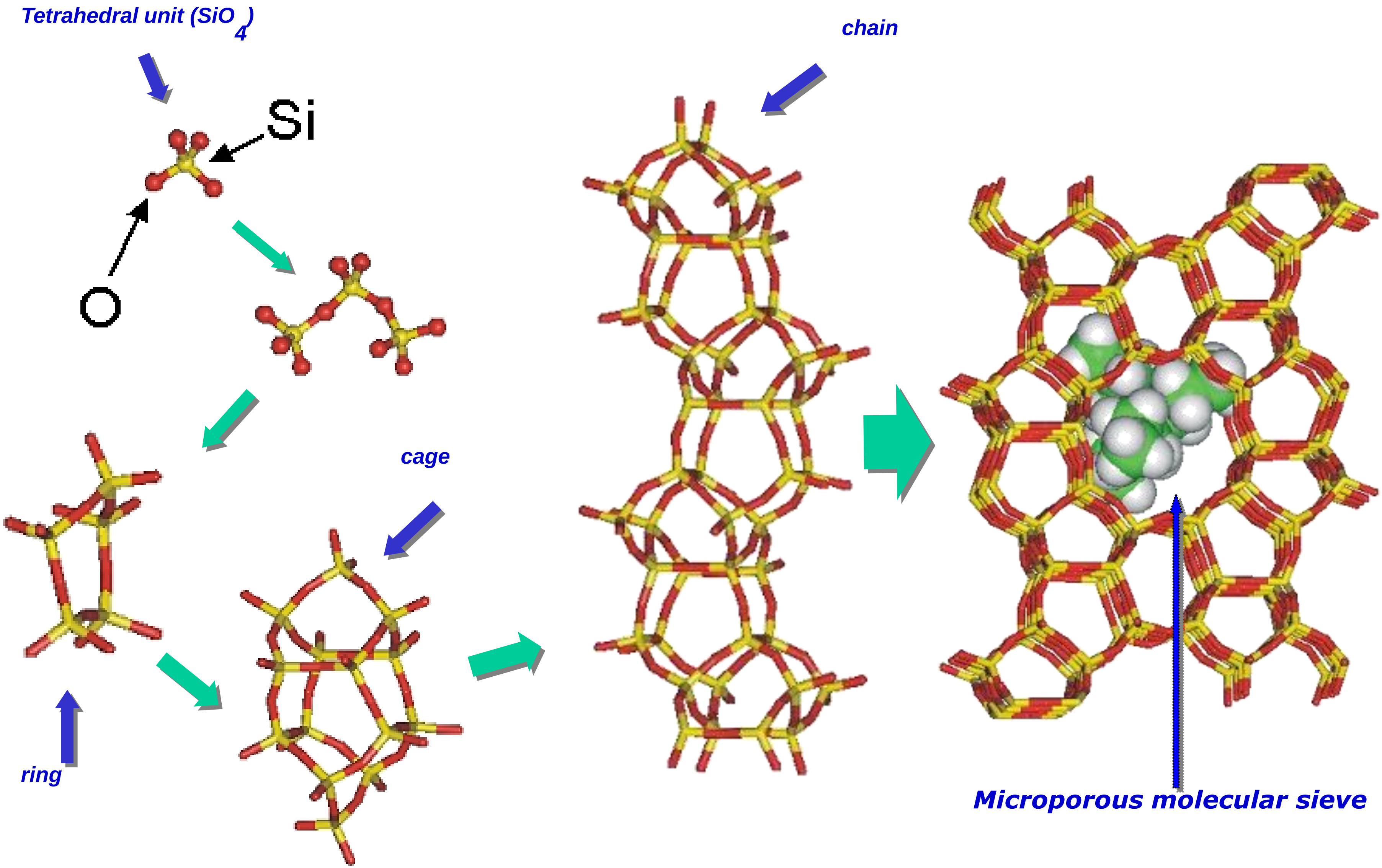

(a)
Normalized μ·x
Normalized Δμ·x
Energy (eV)
0 mbar
1 mbar
10 mbar
17 mbar
20 mbar
25 mbar
100 mbar
1000 mbar
(b)
k²χ(k) (Å⁻²)
k (Å⁻¹)
J. Phys. Chem. C 2017, 121, 18202−18213
Scattered intensity (a.u.)
2θ (degrees)
0 mbar
1 mbar
10 mbar
17 mbar
20 mbar
25 mbar
100 mbar
1000 mbar

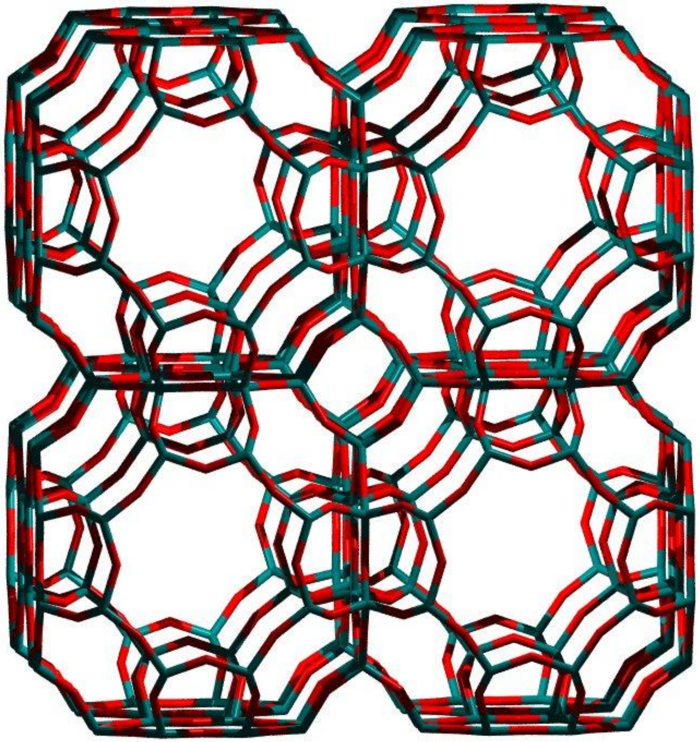
J. Phys. Chem. C 2017, 121, 18202−18213



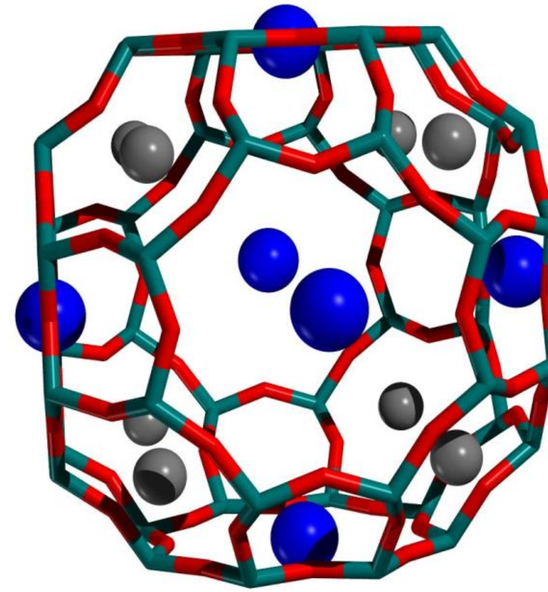


The building-up of a zeolitic framework

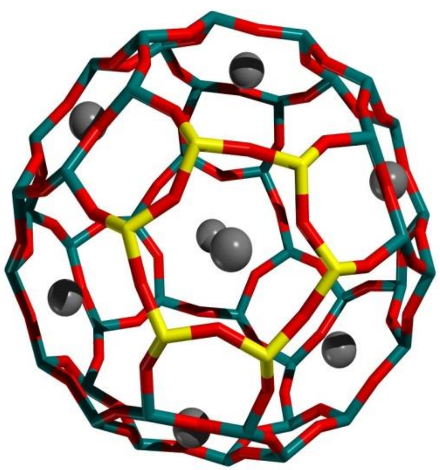


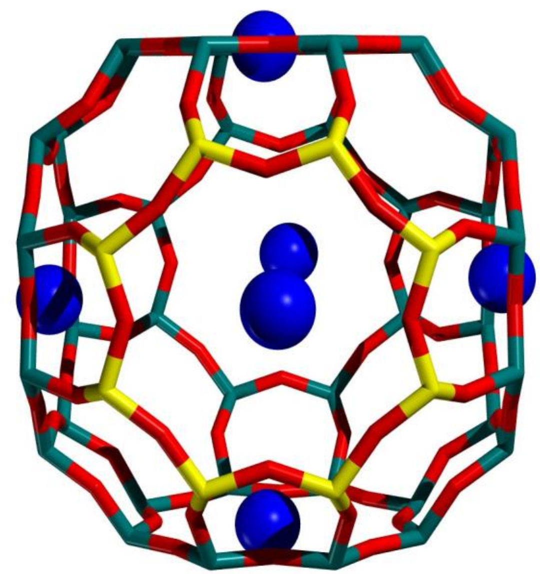


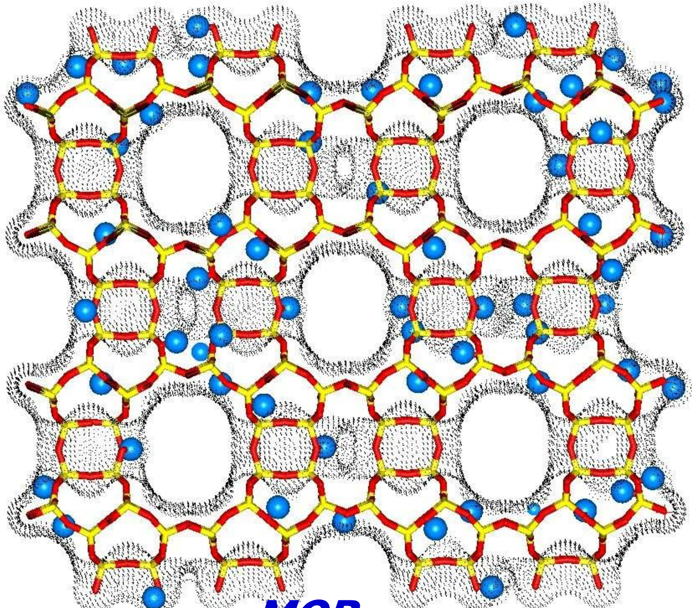
Sodalite



Linde Type A

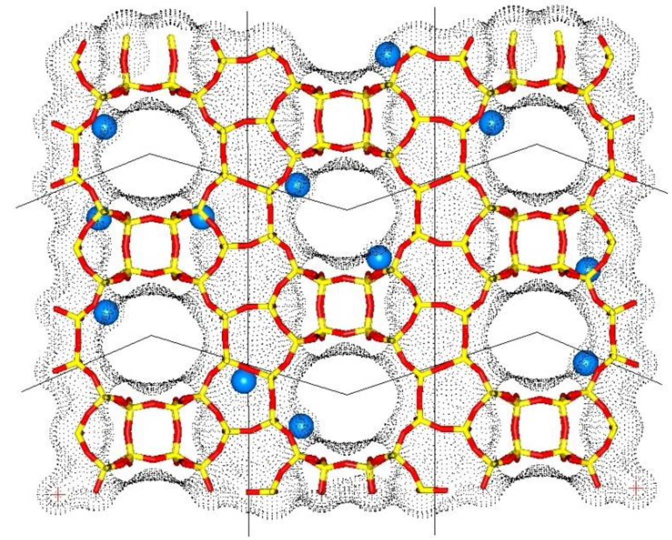




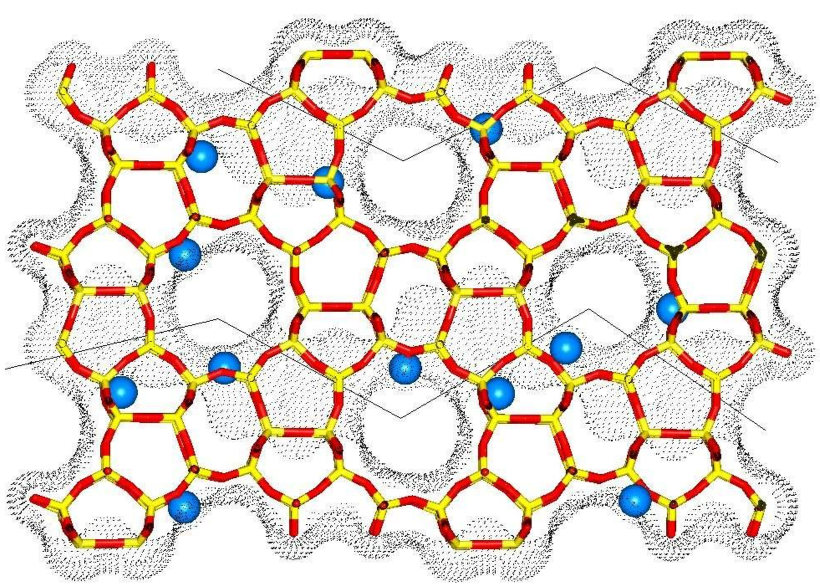


MOR

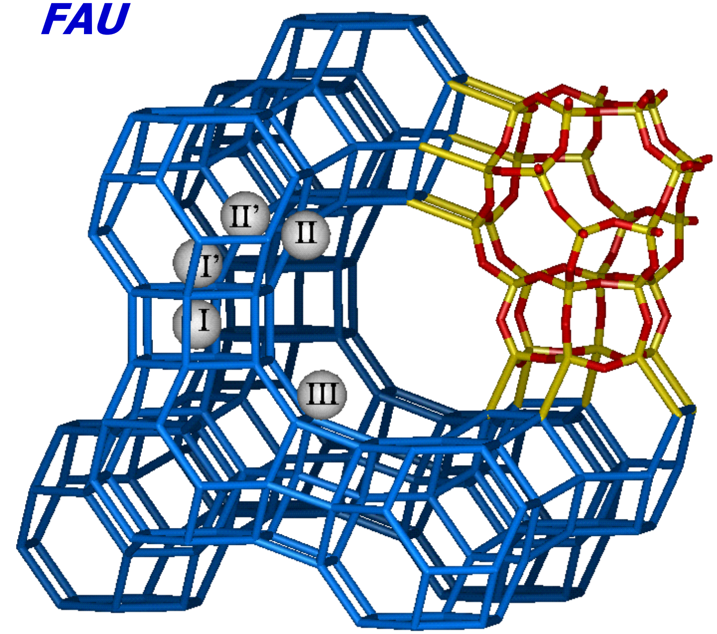
BEA

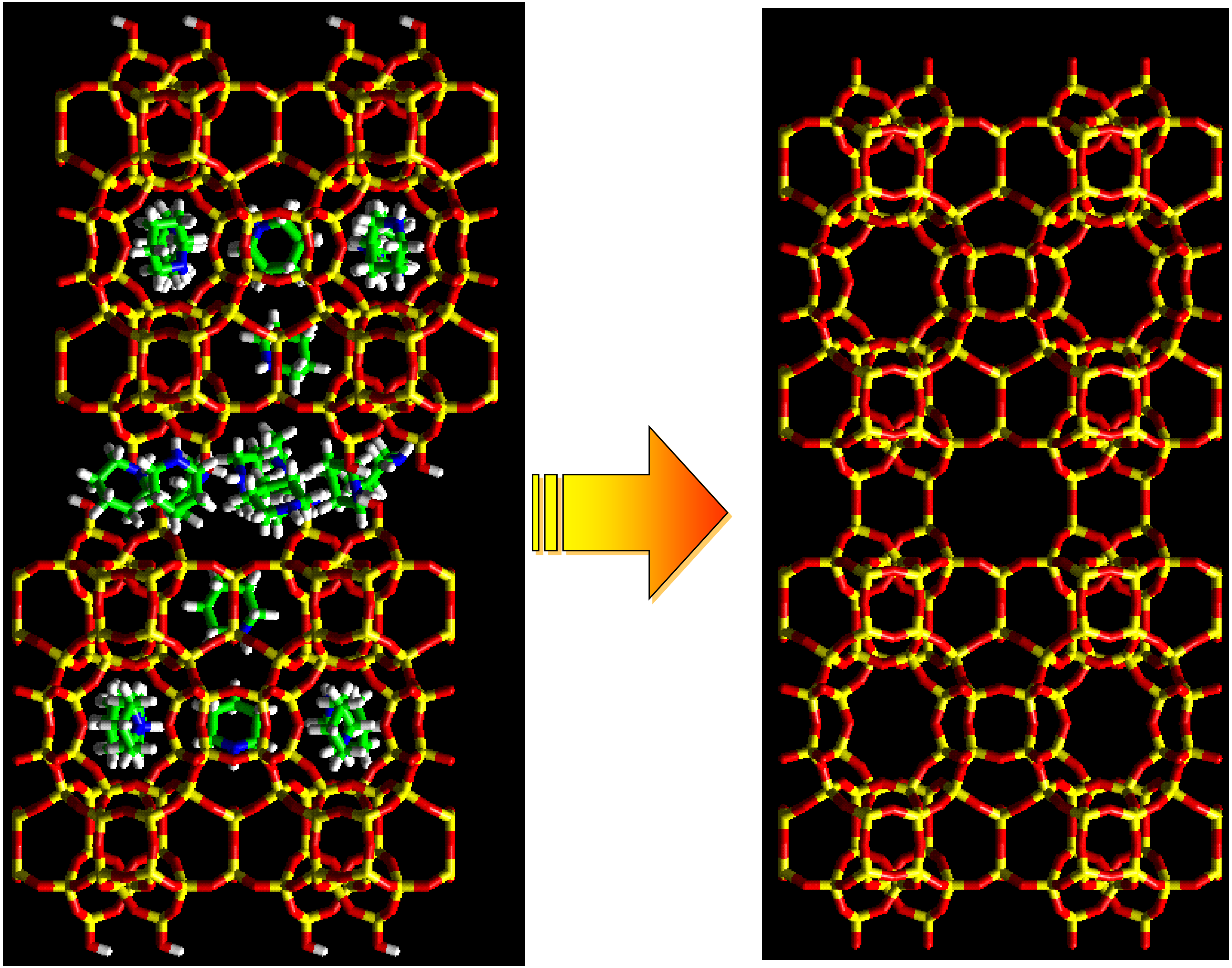


MFI



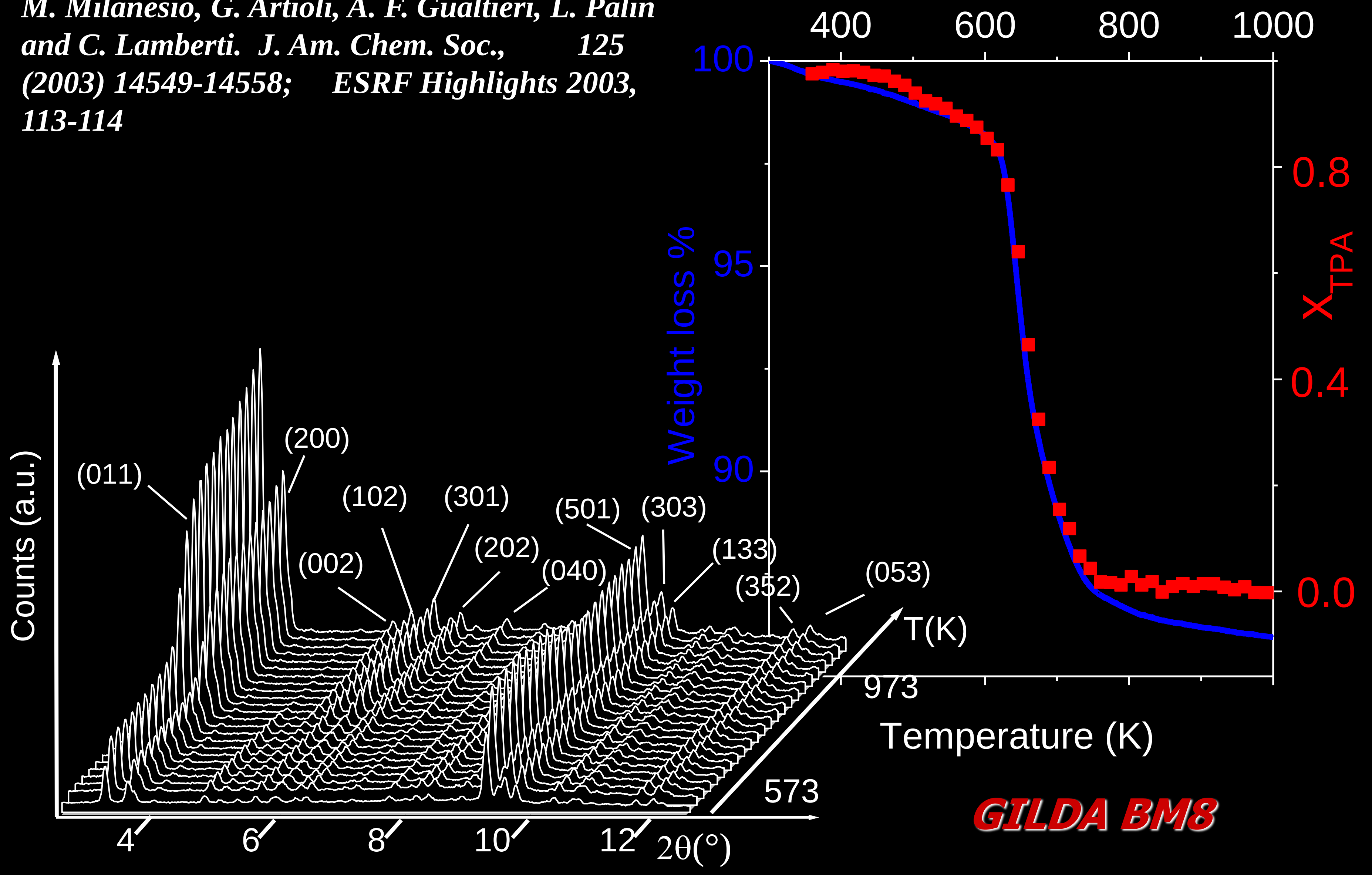
FAU



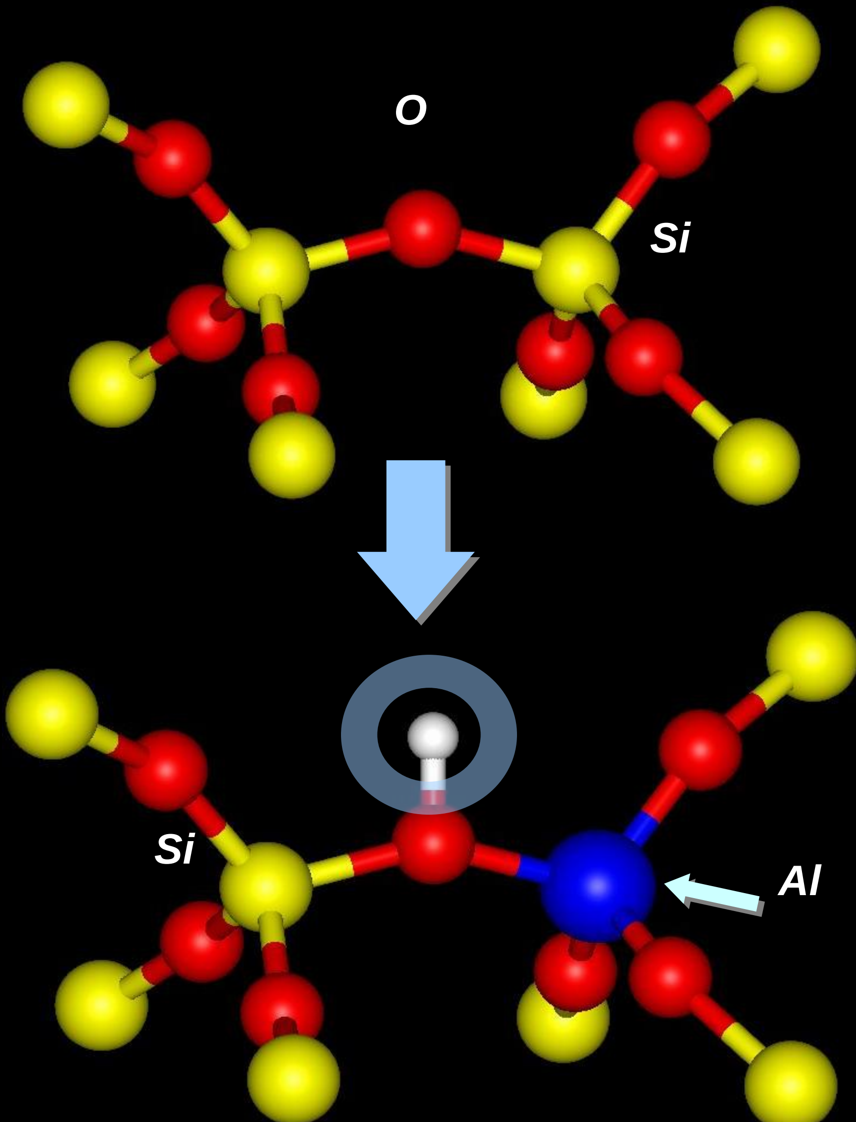
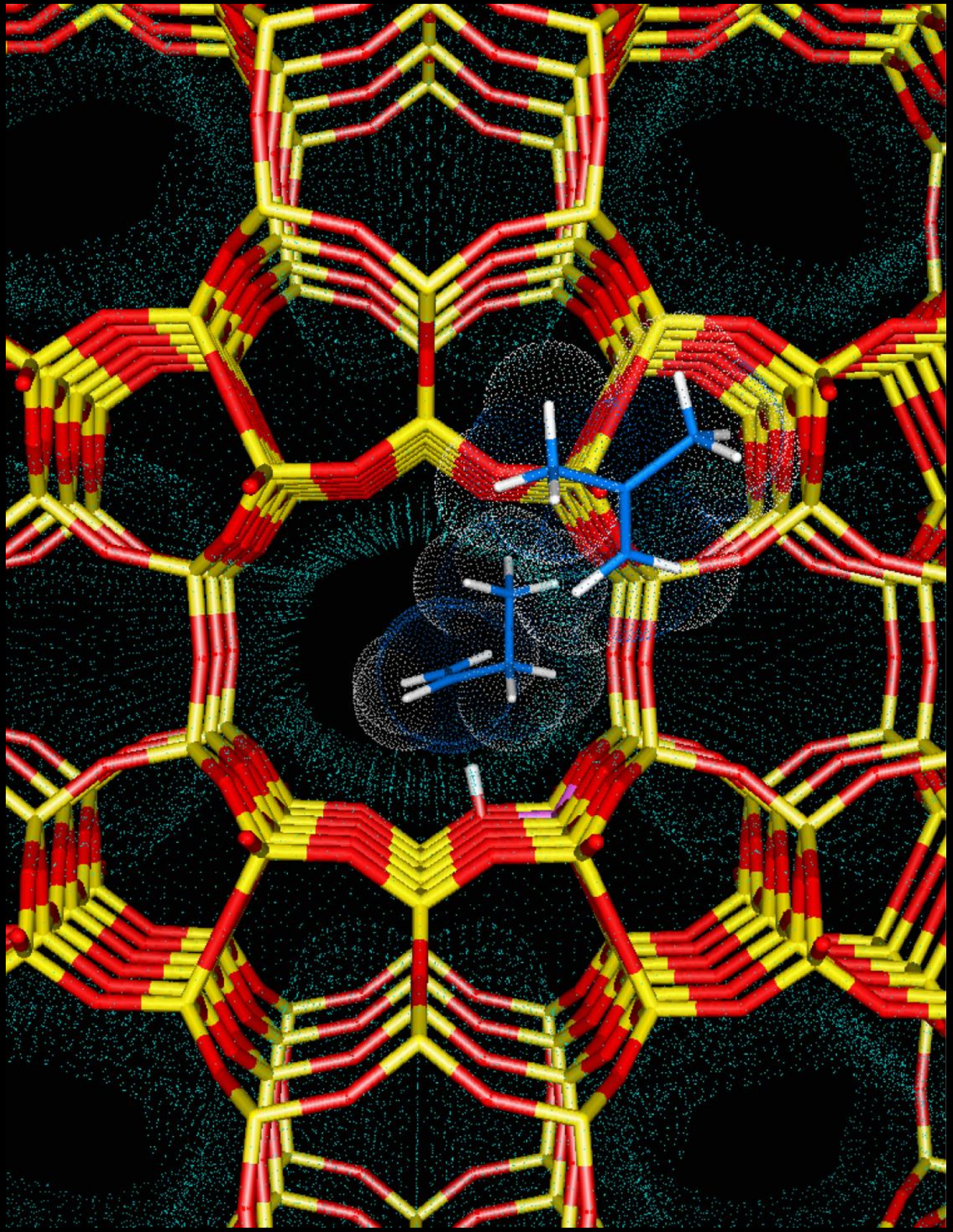


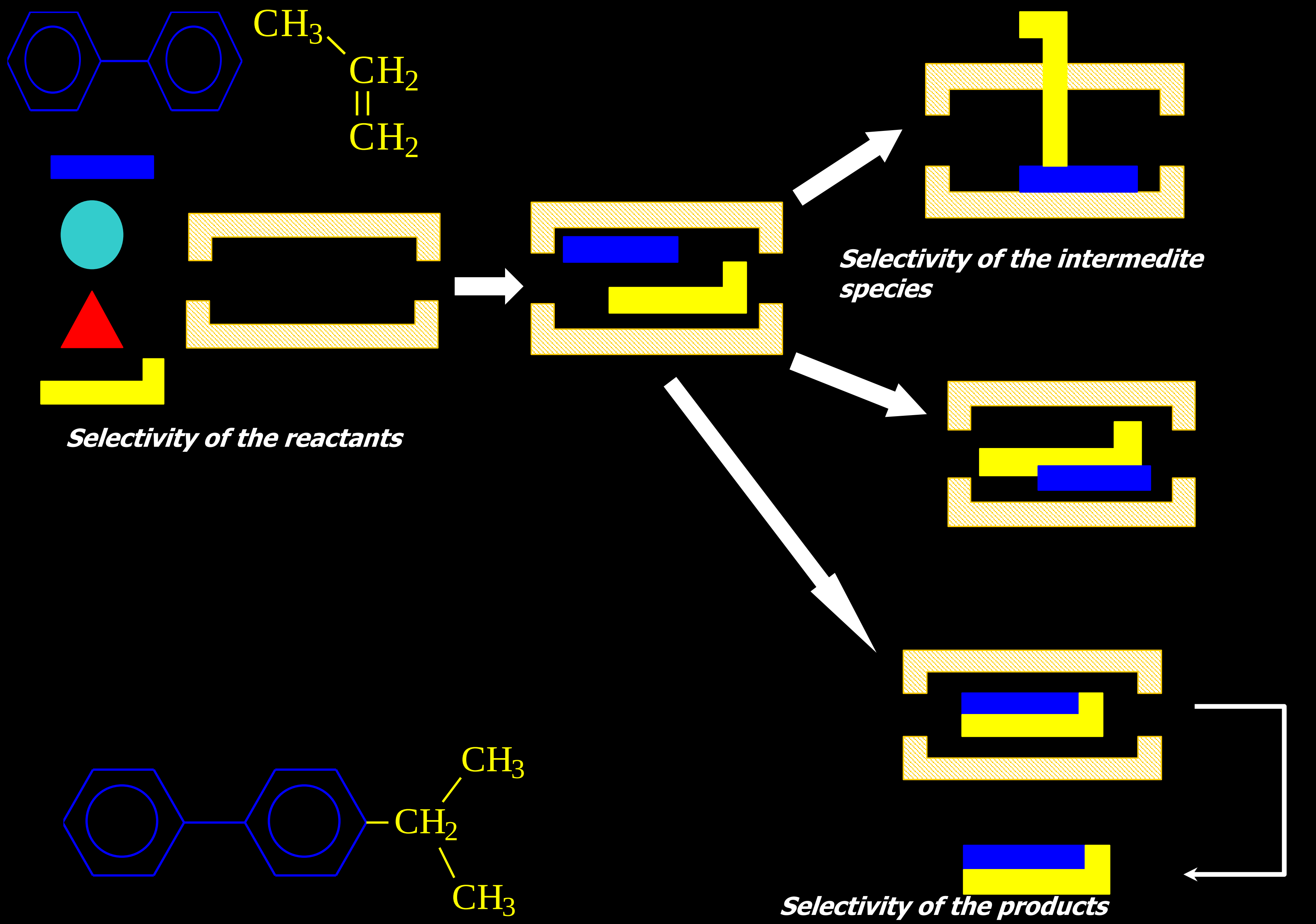
In situ template burning by XRPD

M. Milanesio, G. Artioli, A. F. Gualtieri, L. Palin and C. Lamberti. J. Am. Chem. Soc., 125 (2003) 14549-14558; ESRF Highlights 2003, 113-114



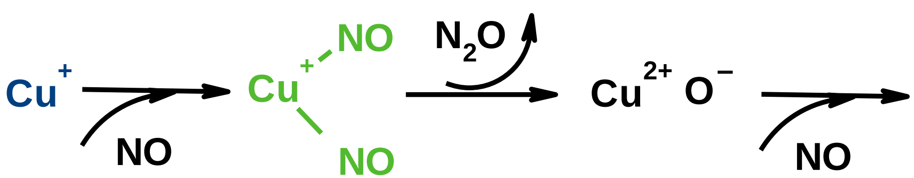
GILDA BM8

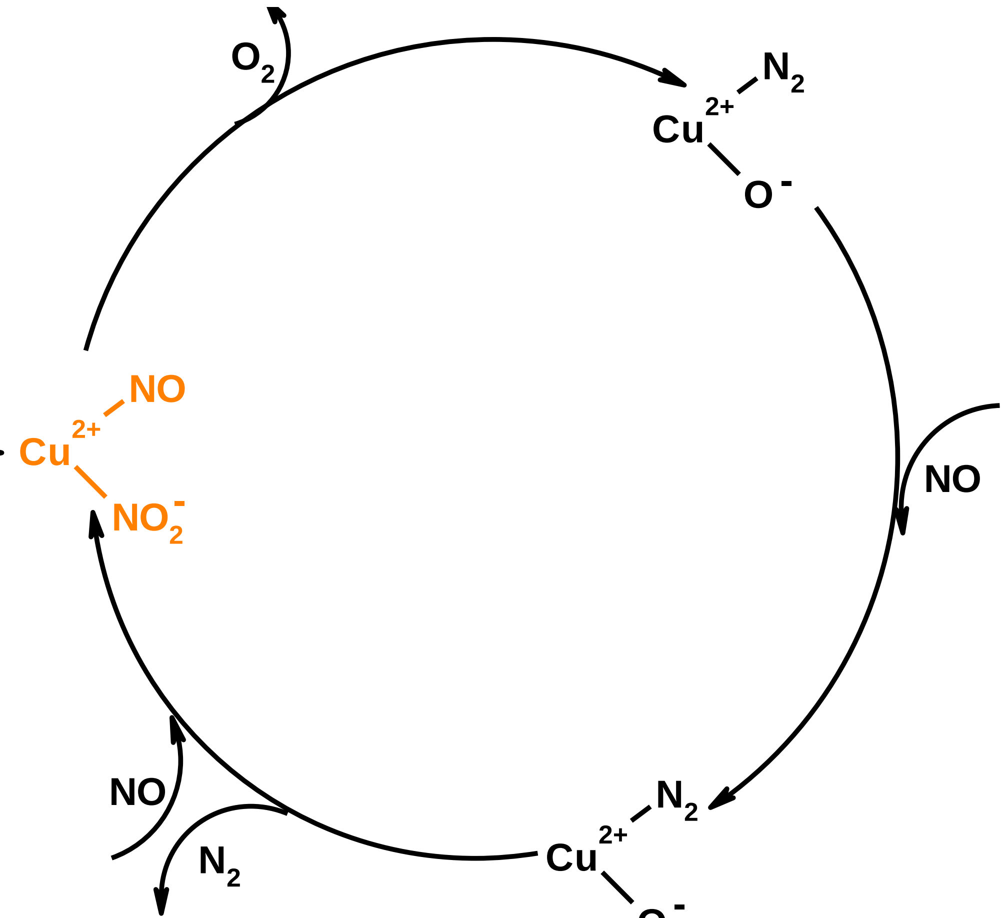

O
Si
Si
Al



CH3
CH2
CH2
Selectivity of the reactants
Selectivity of the intermedite species
Selectivity of the products
CH3
CH2
CH3

Cu+-zeolites: Interests & Applications

Iwamoto & Hamada, Catal. Today 1991, 10, 57
Lamberti et al, J. Phys. Chem. B, 1997, 101 , 344



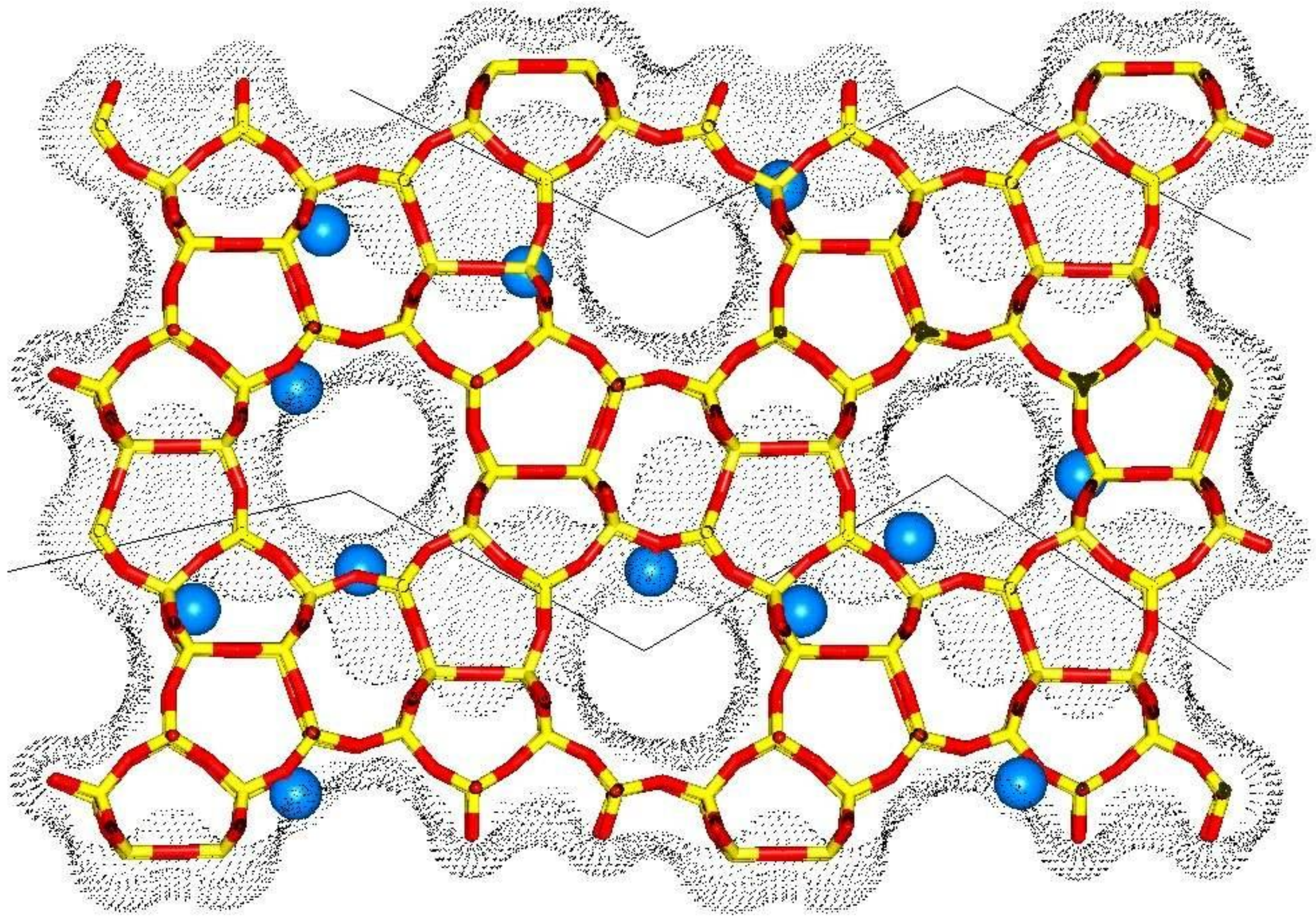


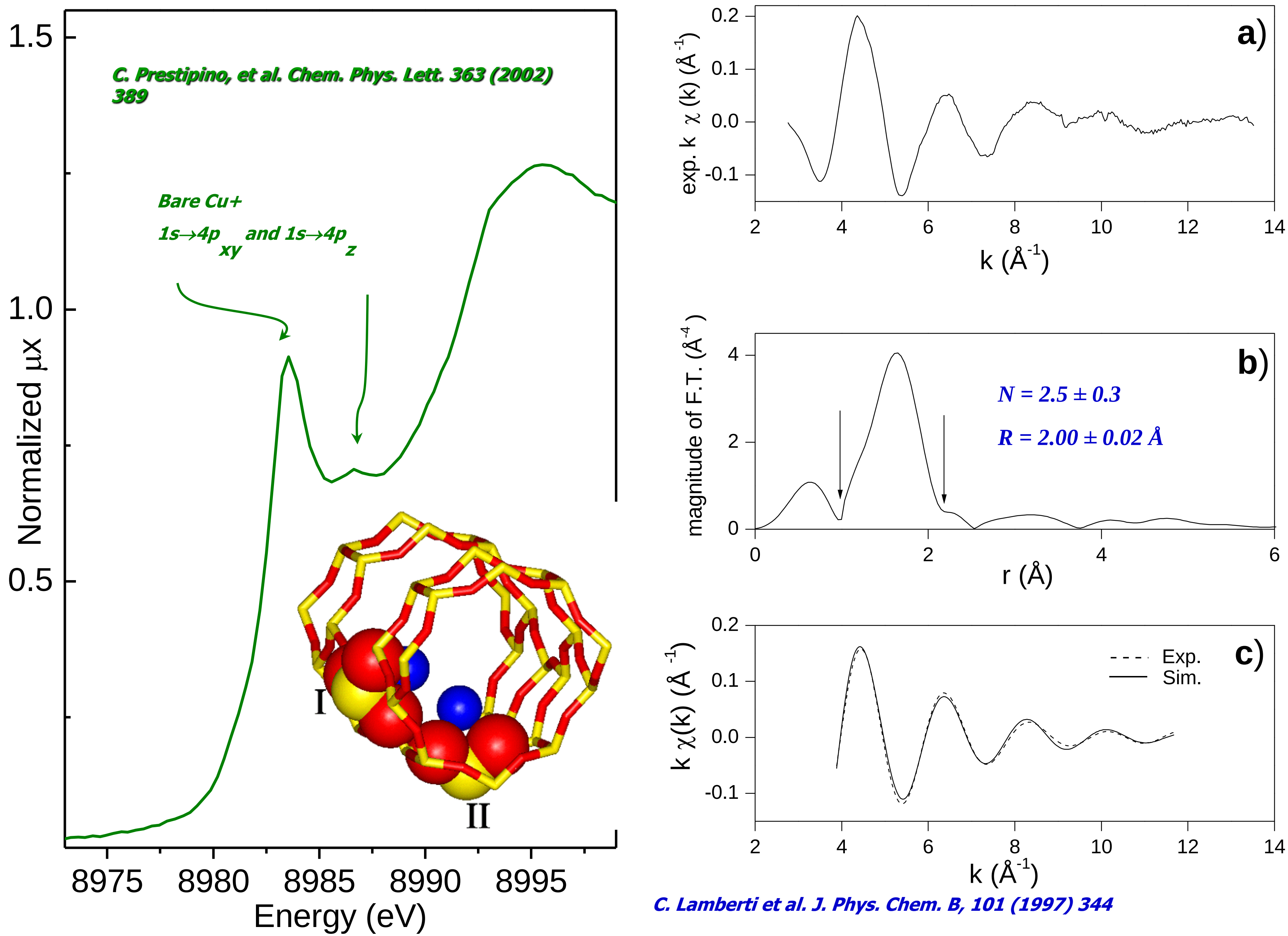
Cu-exchanged zeolites are very

active catalysts for the direct conversion of NOx into O_2 and N_2

Prestipino et al., Chem. Phys. Lett., 2002, 363 , 389
Llabrés i Xamena et al., J. Phys. Chem. B, 2003, 107, 7036

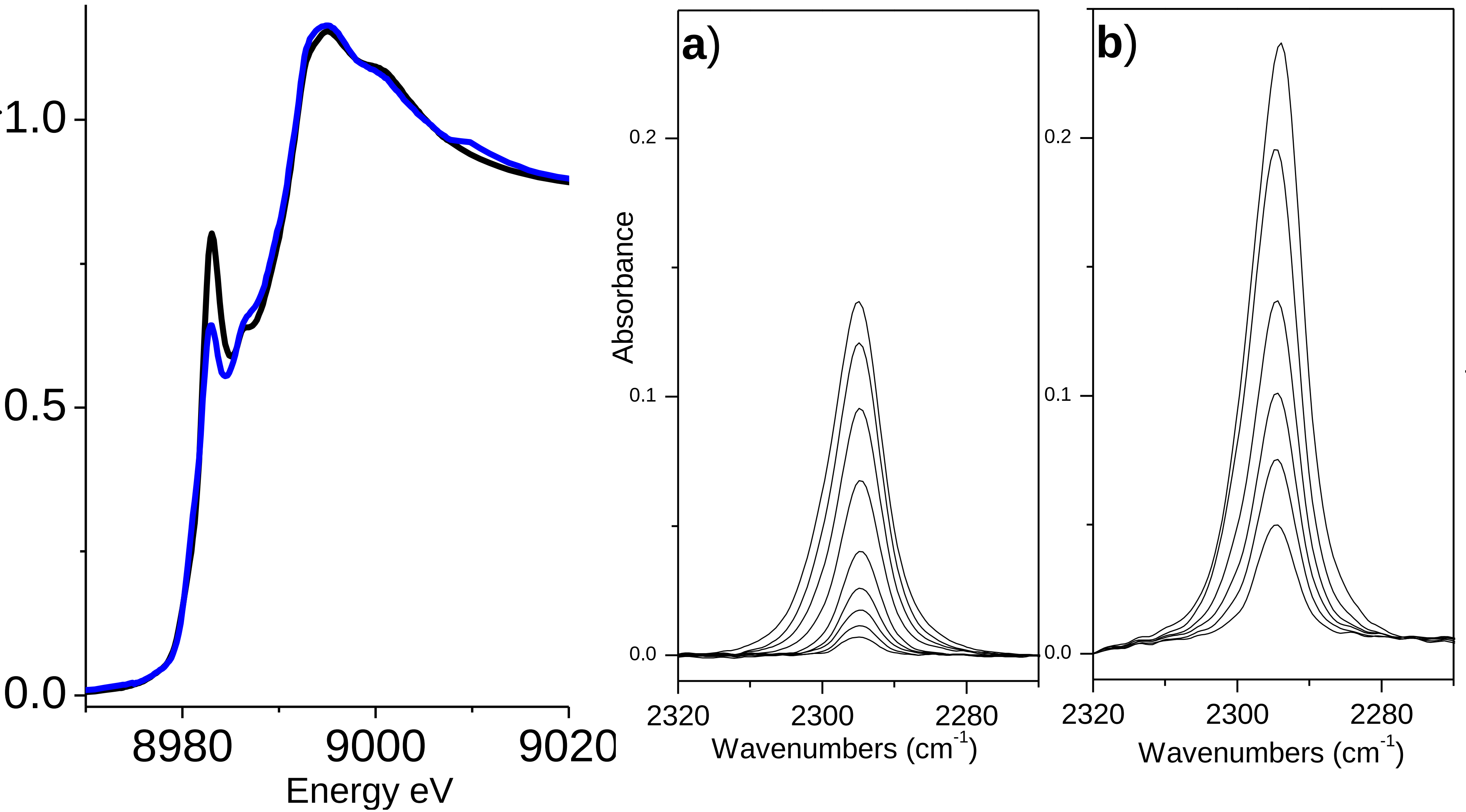
MFI





C. Prestipino, et al. Chem. Phys. Lett. 363 (2002) 389
Bare Cu+
1s→4pxy and 1s→4pz
Normalized μx
1.5
1.0
0.5
8975
8980
8985
8990
8995
Energy (eV)
I
II
a)
exp. k χ (k) (Å-1)
k (Å-1)
b)
magnitude of F.T. (Å-4)
r (Å)
N = 2.5 ± 0.3
R = 2.00 ± 0.02 Å
c)
k χ(k) (Å-1)
Exp.
Sim.
k (Å-1)
C. Lamberti et al. J. Phys. Chem. B, 101 (1997) 344

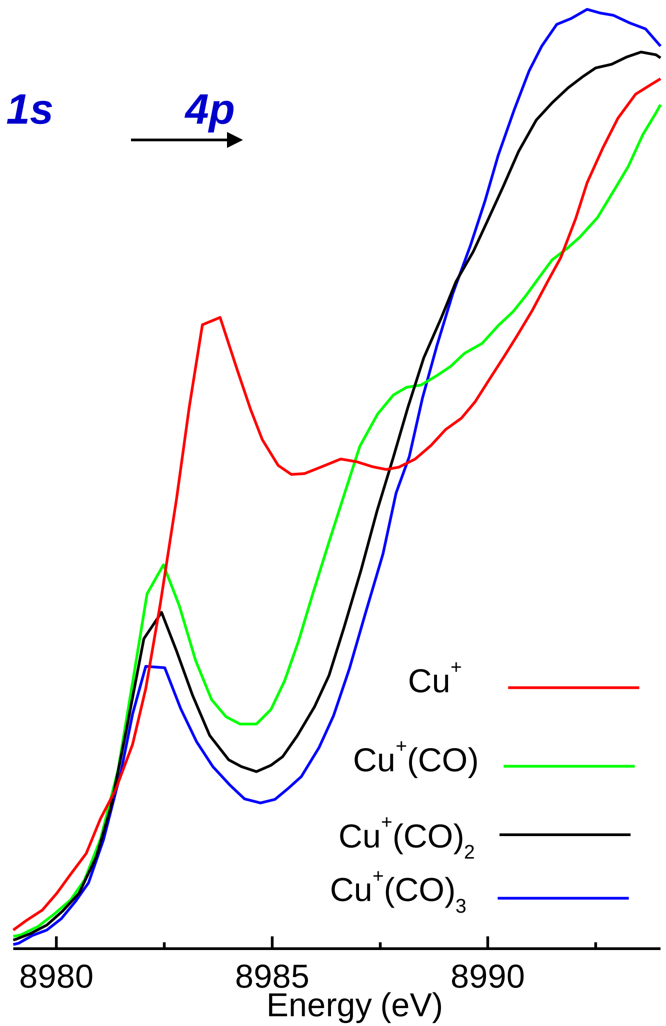
N_2 on Cu+-ZSM-5

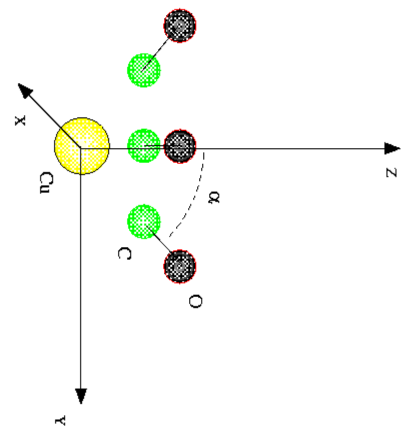


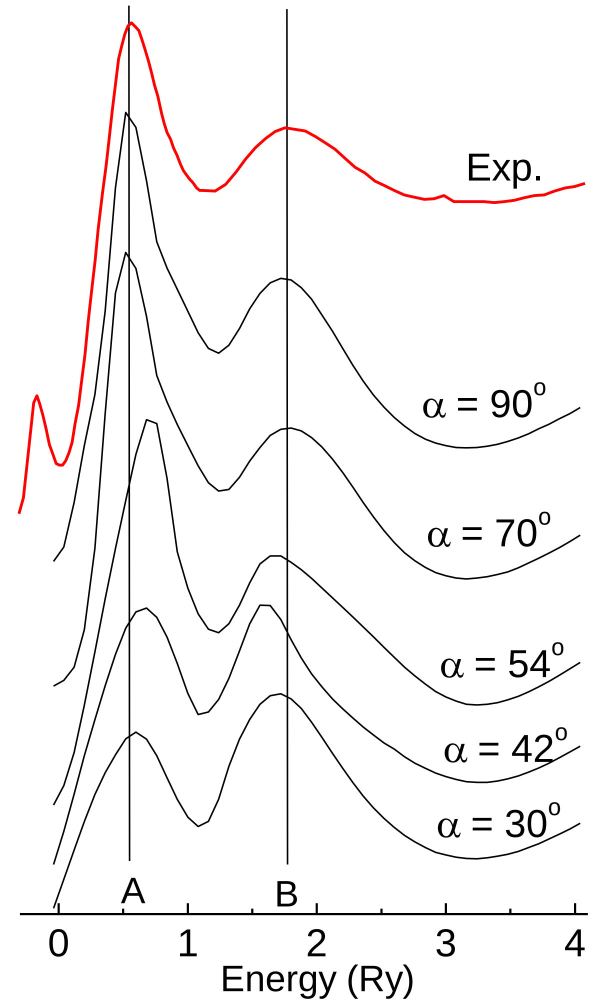
C. Lamberti et al. J. Phys. Chem. B, 101 (1997) 344

C. Lamberti et al. Phys. Chem. Chem. Phys., 5 (2003) 4502

Geometry of the $Cu^{+}(CO)_3$ complex in ZSM-5: XANES spectra



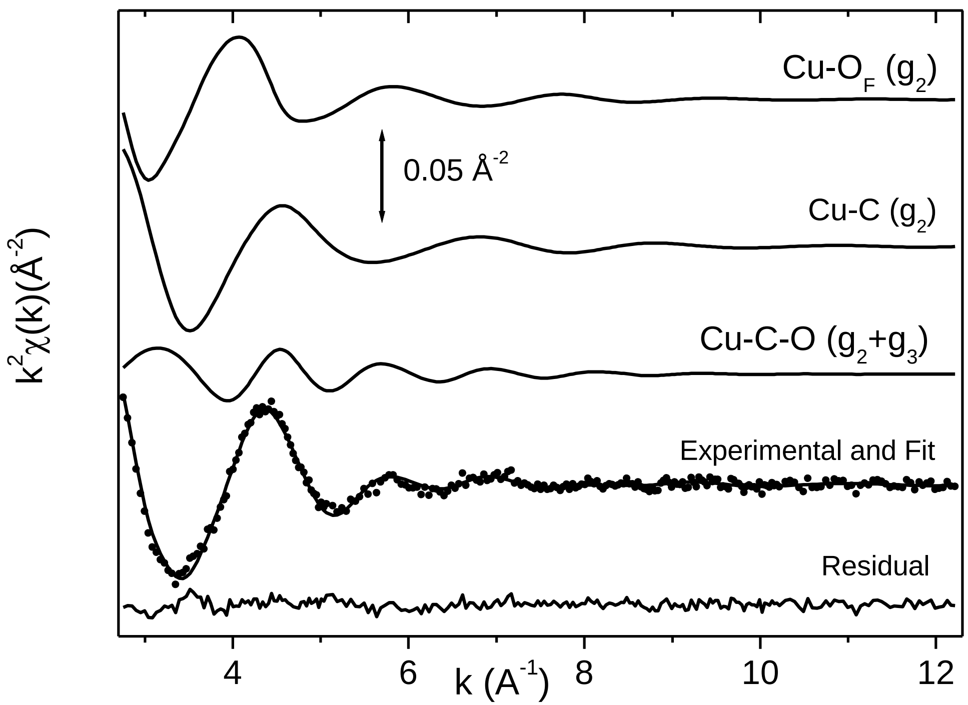


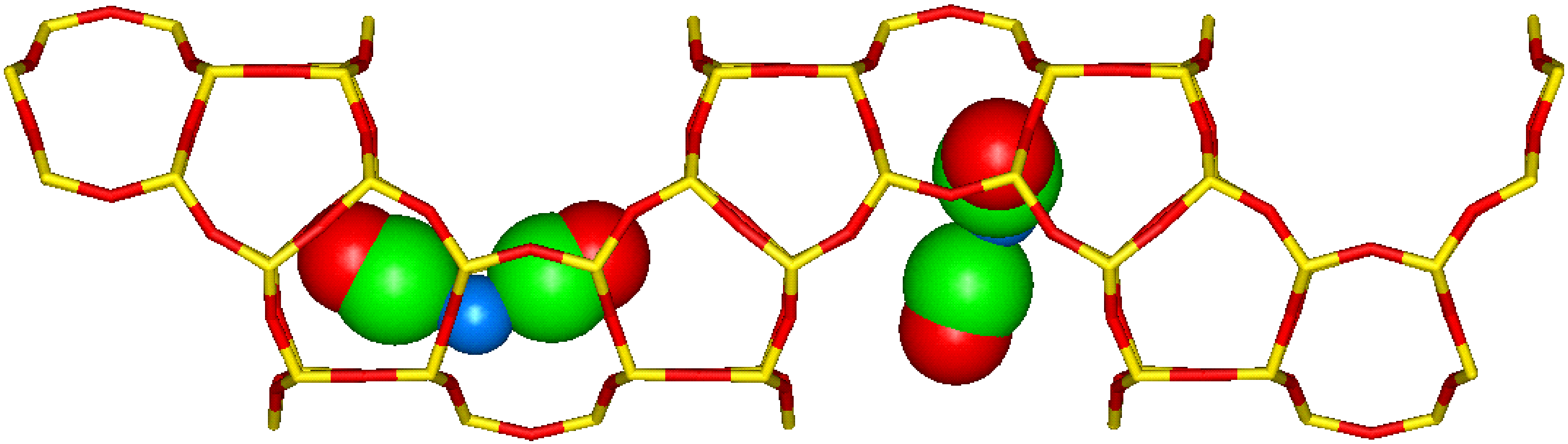


Formation of $CuI(CO)_n$ → electron transfer from CO to CuI

C. Lamberti, et al. Angew. Chem. Int. Ed., 39 (2000) 2138-2141

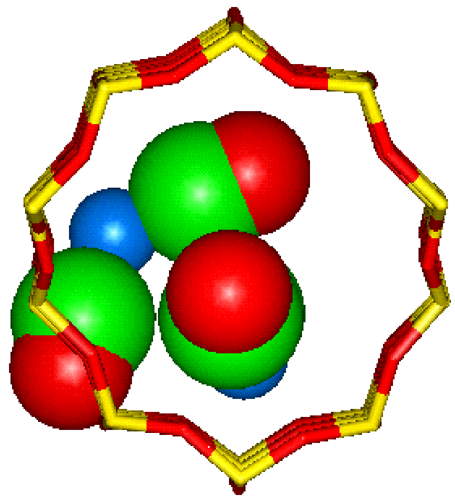
Local structure of [CuI(CO)$_2$]+ *adducts hosted inside ZSM-5 zeolite*

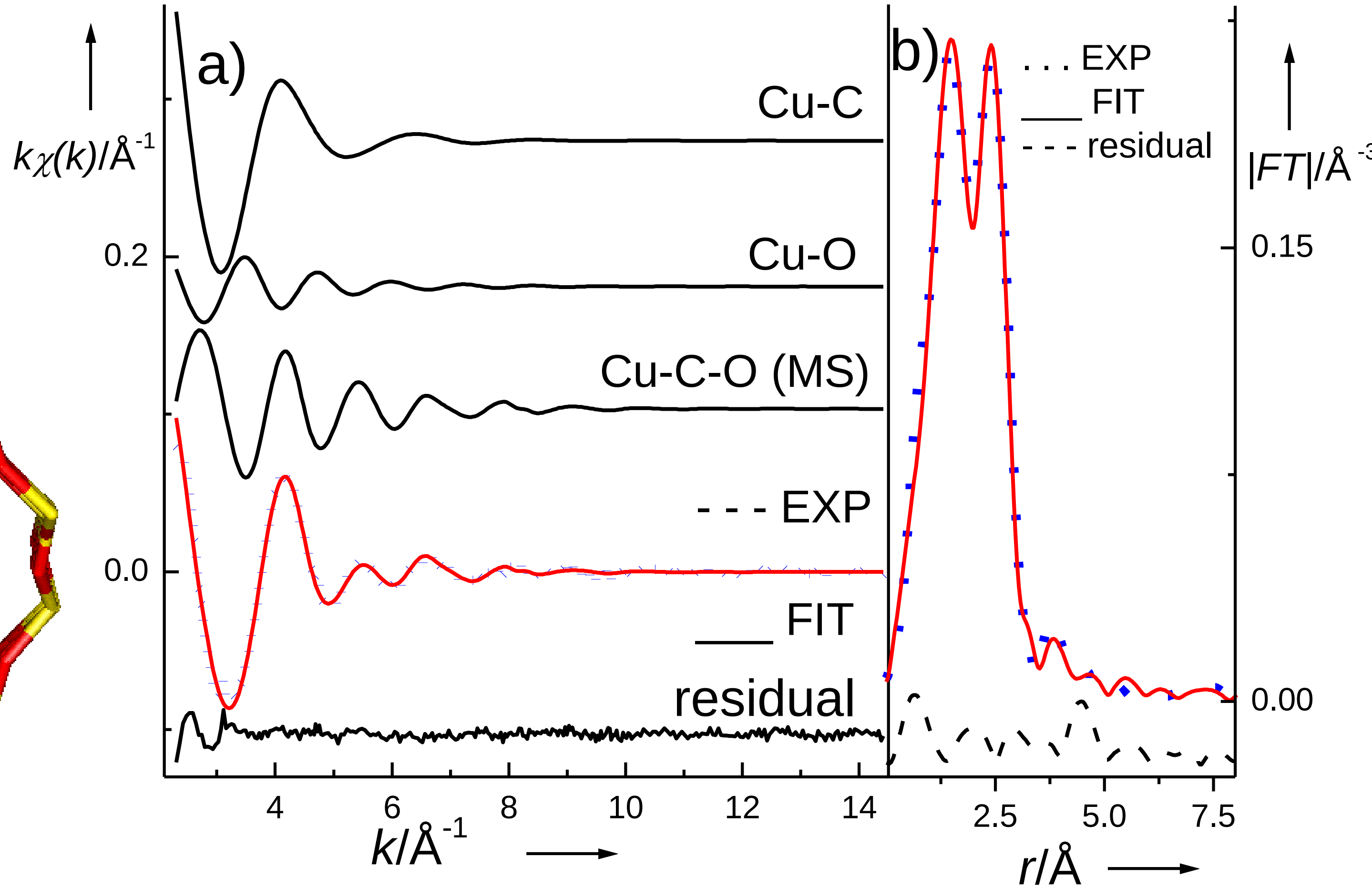




C. Prestipino, et al. Phys. Chem. Chem. Phys., 7 (2005) 1743

Local structure of [CuI(CO)$_3$]+ adducts hosted inside ZSM-5 zeolite



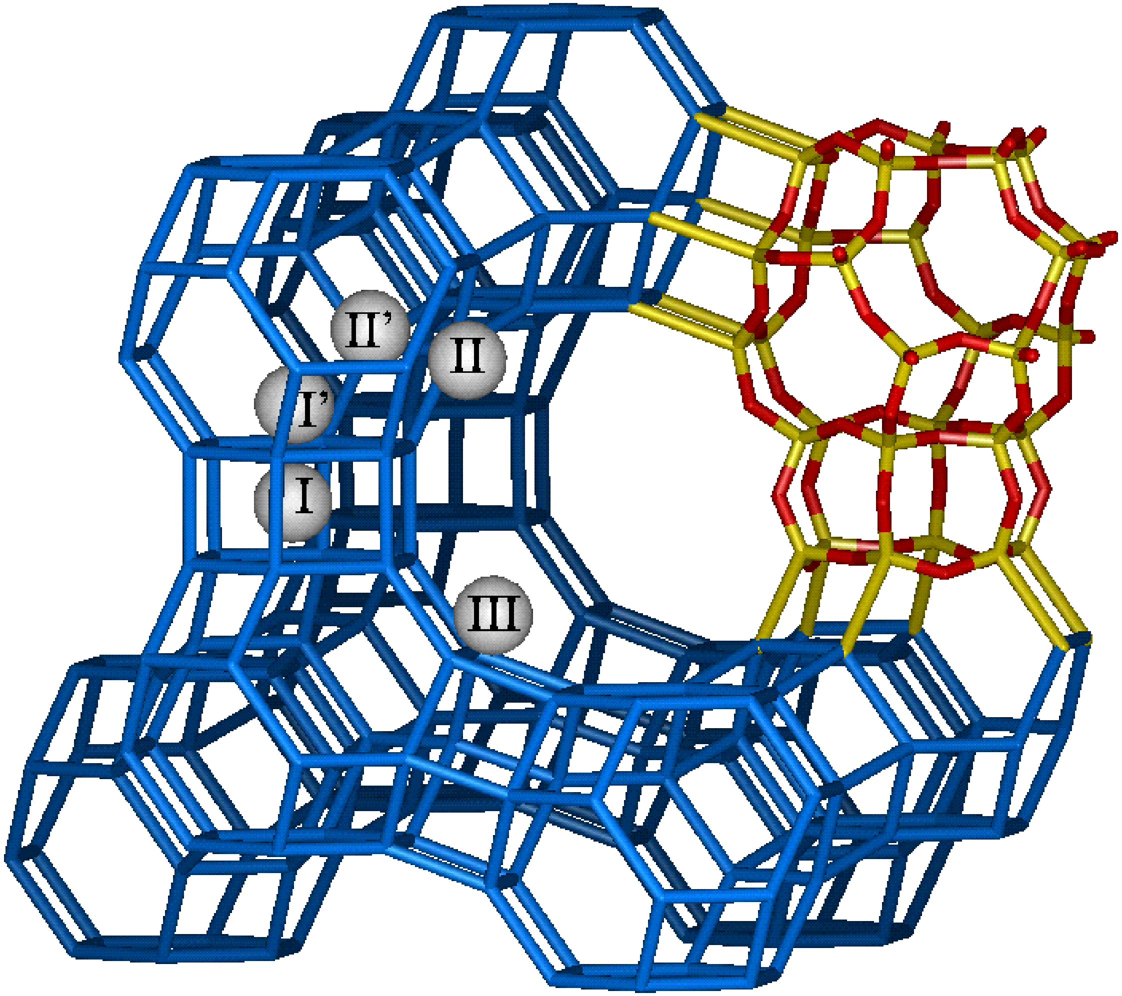


Cu$^+$ complexes	N_{CO}	R_{Cu-OF} (Å)	R_{Cu-C} (Å)	R_{C-O} (Å)	θ_{Cu-C-O} (°)
Cu$^+$	–	2.00 ± 0.02	–	–	–
Cu+(CO)$_2$	1.8 ± 0.3	2.11 ± 0.03	1.88 ± 0.02	1.12 ± 0.03	170 ± 10
Cu$^+$(CO)$_3$	3 (fixed)	–	1.93 ± 0.02	1.12 ± 0.03	180 ± 10

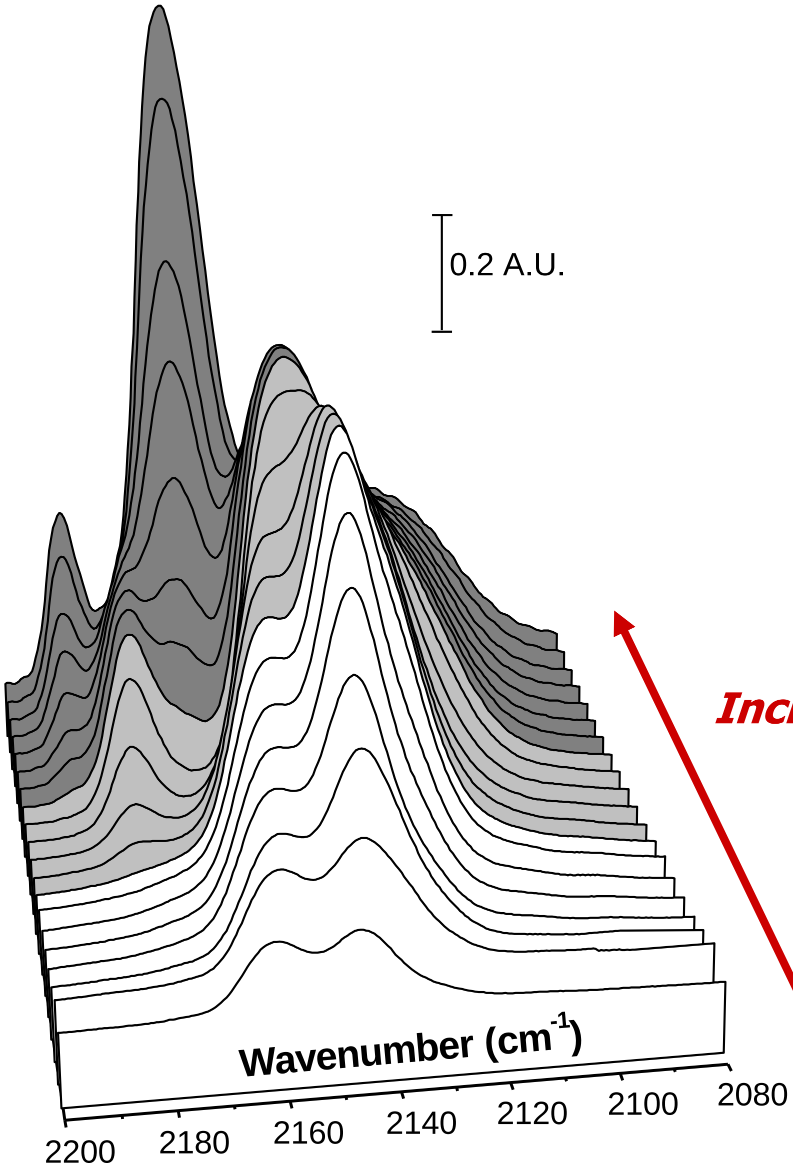
C. Prestipino, et al. PCCP., 7 (2005) 1743

C. Lamberti, et al. Angew. Chem. Int. Ed., 39 (2000) 2138

Y



Cu+-Y: IR spectroscopy of CO at 80 K



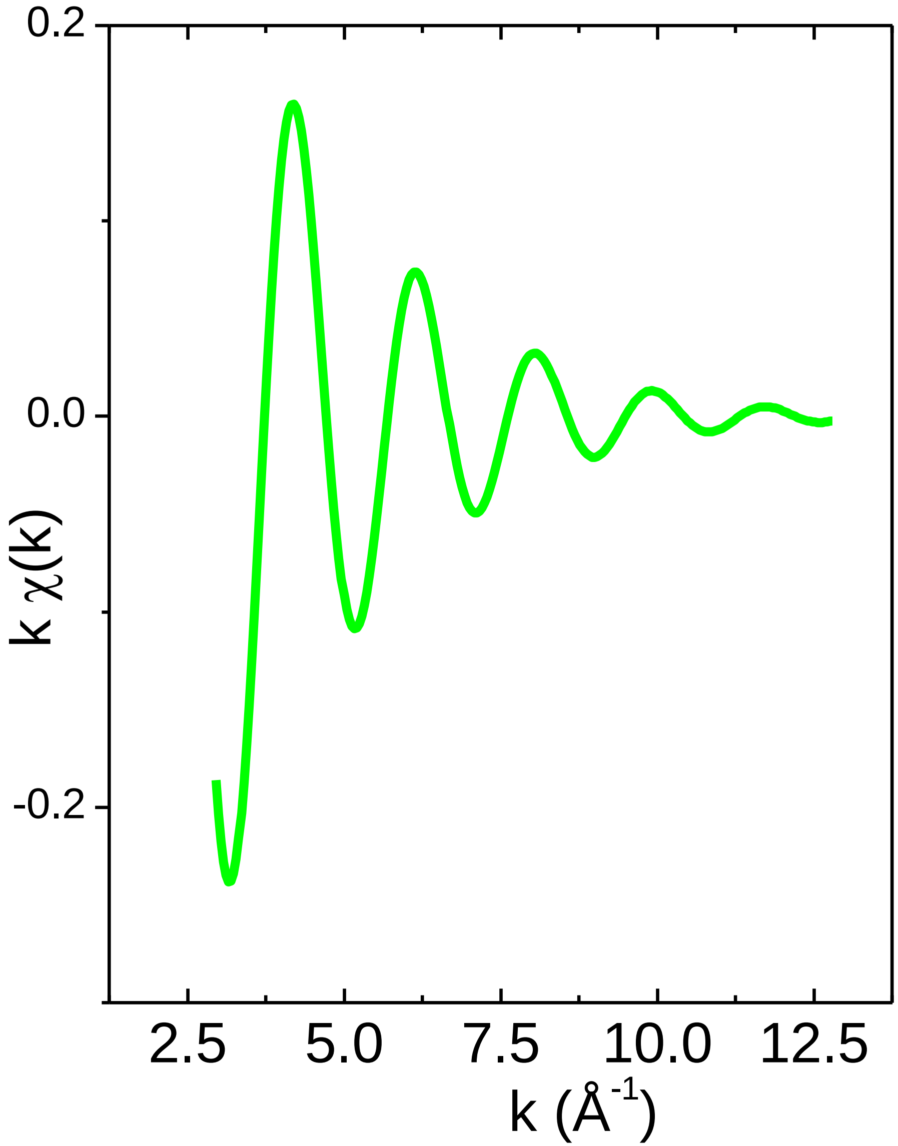
Low P_{CO} 2 bands: 2 Cu+ sites?

Medium P_{CO} 4 bands: 4 Cu+ sites?

High P_{CO} 3 bands: ???????????

Increasing P_{CO}

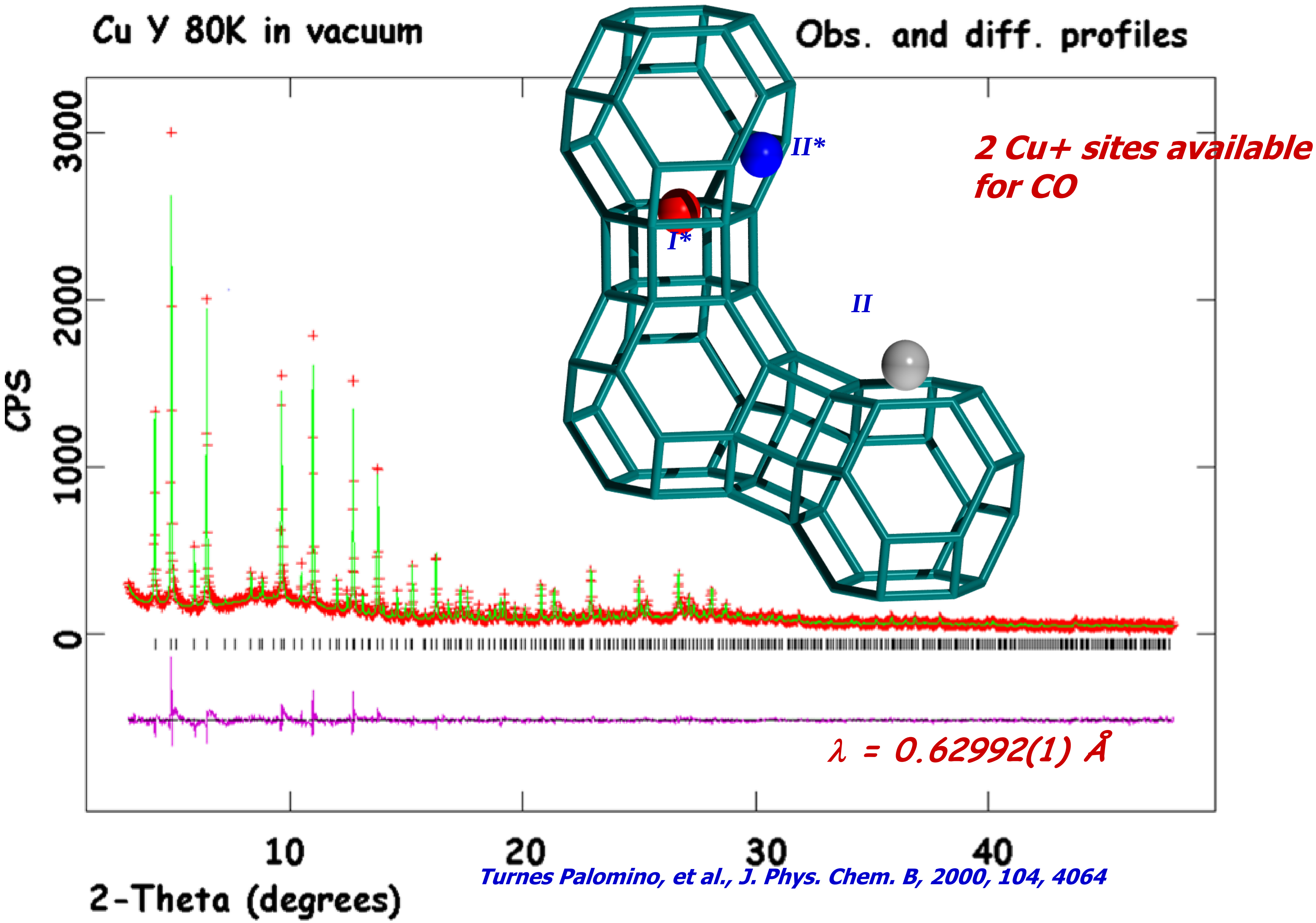
Cu+-Y:EXAFS data: GILDA BM8 @ ESRF



It was not possible to refine the EXAFS data neither assuming one single Cu+ site nor assuming two different Cu+ environments

Cu+-Y still remains a puzzle

Cu+-Y: in situ XRPD data @ ESRF (80 K)

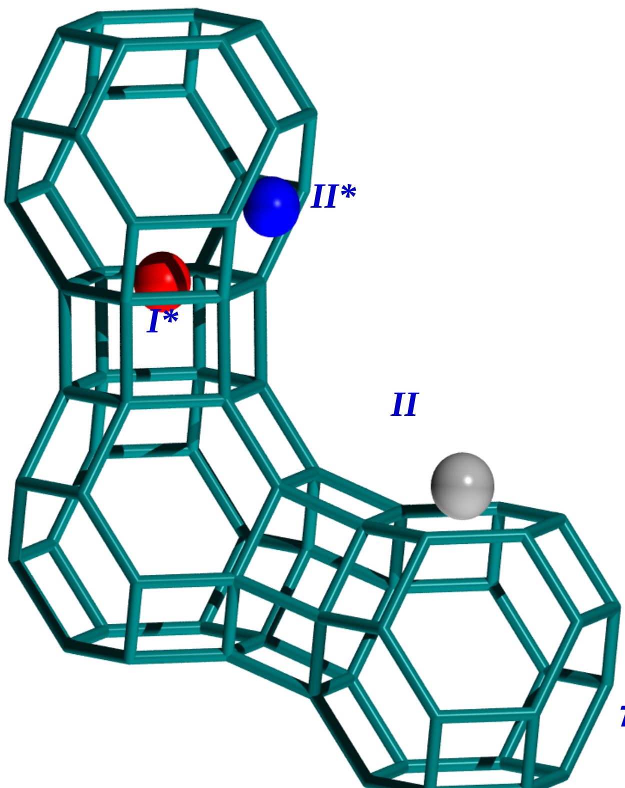


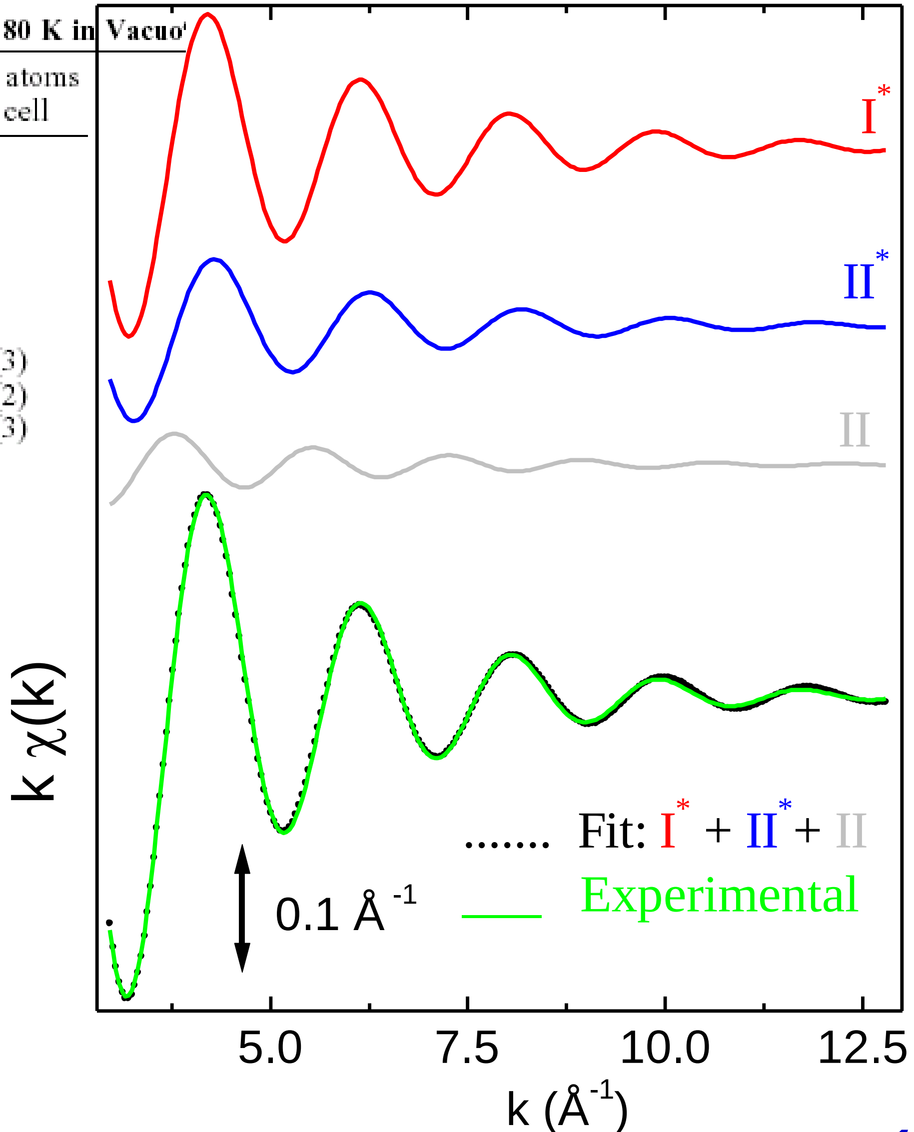
Turnes Palomino, et al., J. Phys. Chem. B, 2000, 104, 4064

Cu+-Y: XRPD explains EXAFS data

Atomic Parameters Resulting from the Rietveld Refinement of the Zeolite at 80 K in Vacuo

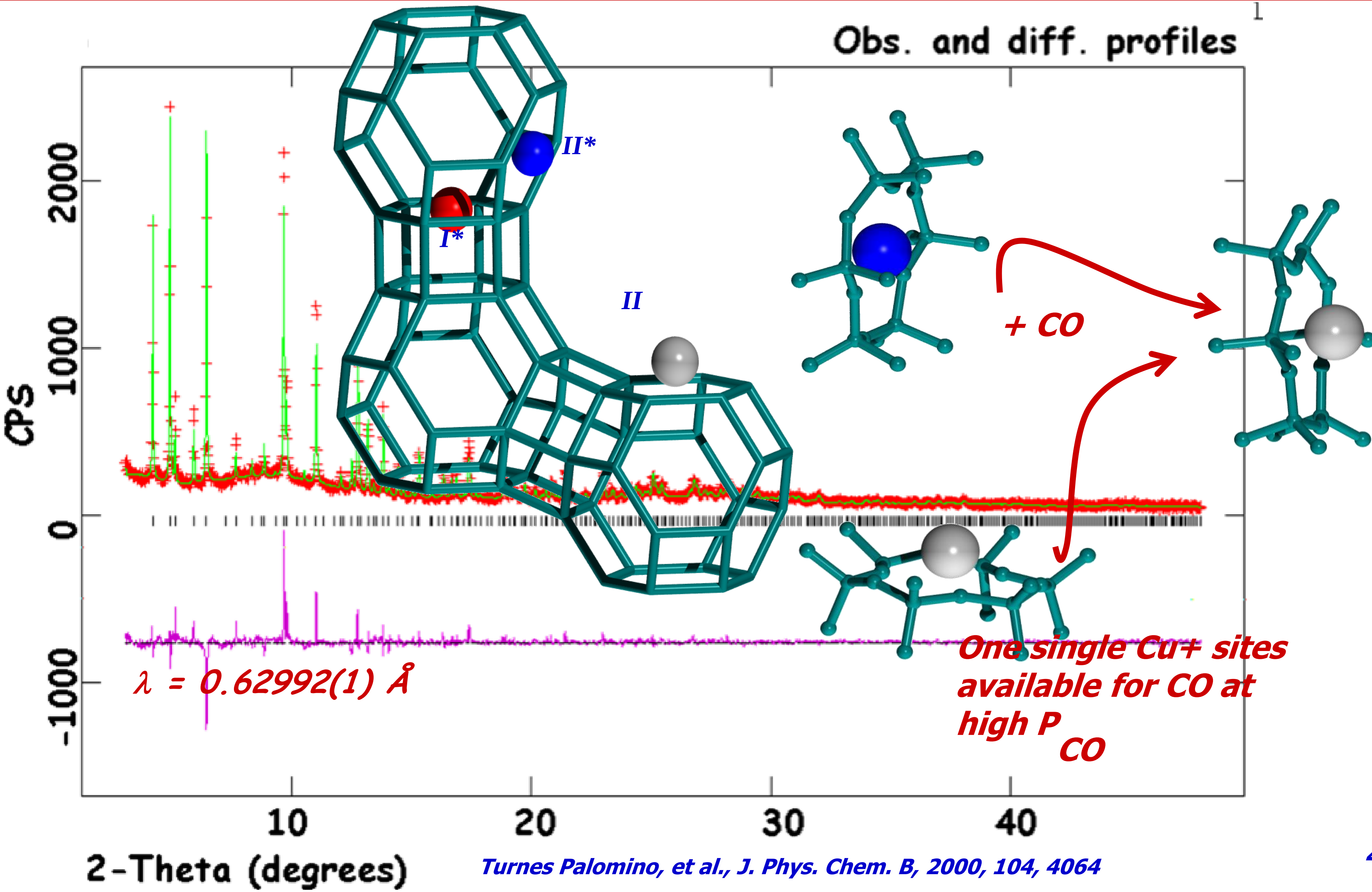
atom	x	y	z	number of atoms per unit cell
Si	0.1238(1)	0.9474(1)	0.0356(1)	140.2
Al	0.1238(1)	0.9474(1)	0.0356(1)	51.8
O1	0.1038(2)	−x	0	96
O2	1.0010(3)	x	0.1484(3)	96
O3	0.1768(2)	x	0.9743(3)	96
O4	0.1732(3)	x	0.3218(4)	96
Cu (II)	0.2360(8)	x	x	6.1(3)
Cu (I*)	0.0377(1)	x	x	23.4(2)
Cu (II*)	0.2171(4)	x	x	11.5(3)





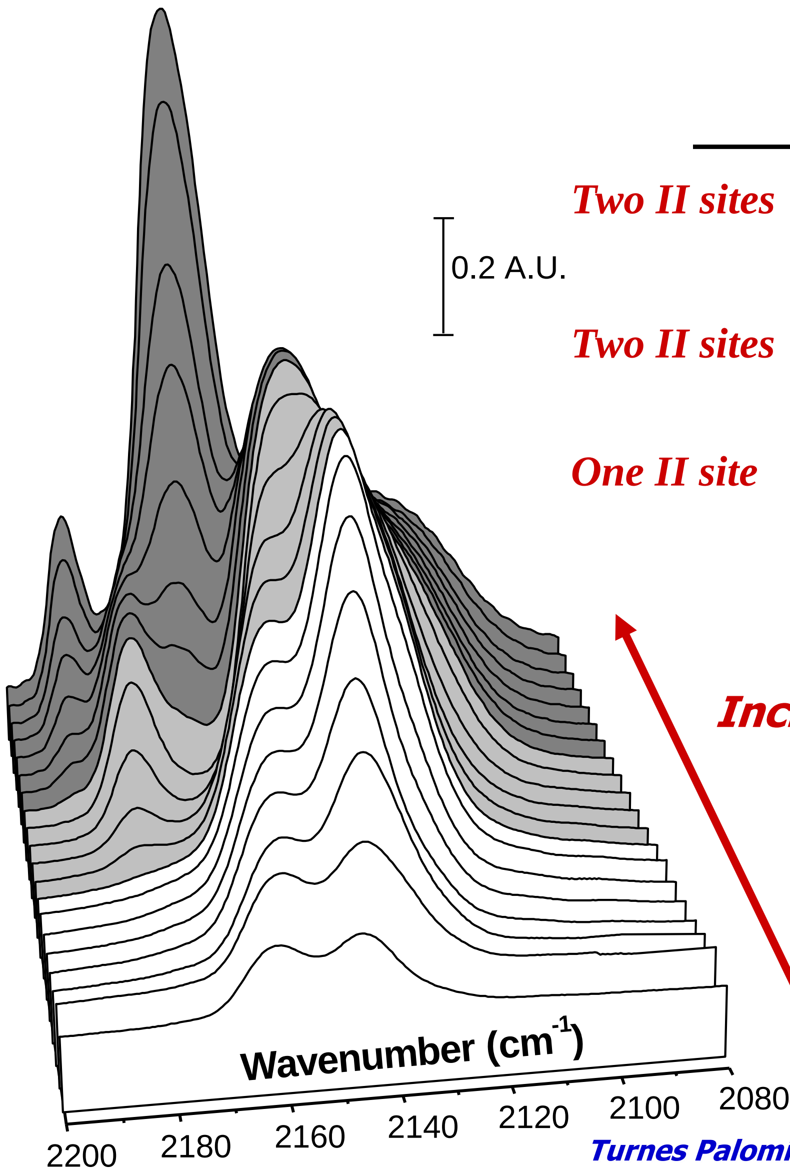
Turnes Palomino, et al., J. Phys. Chem. B, 2000, 104, 4064

Cu+-Y:XRPD interaction with CO at 80 K



Turnes Palomino, et al., J. Phys. Chem. B, 2000, 104, 4064

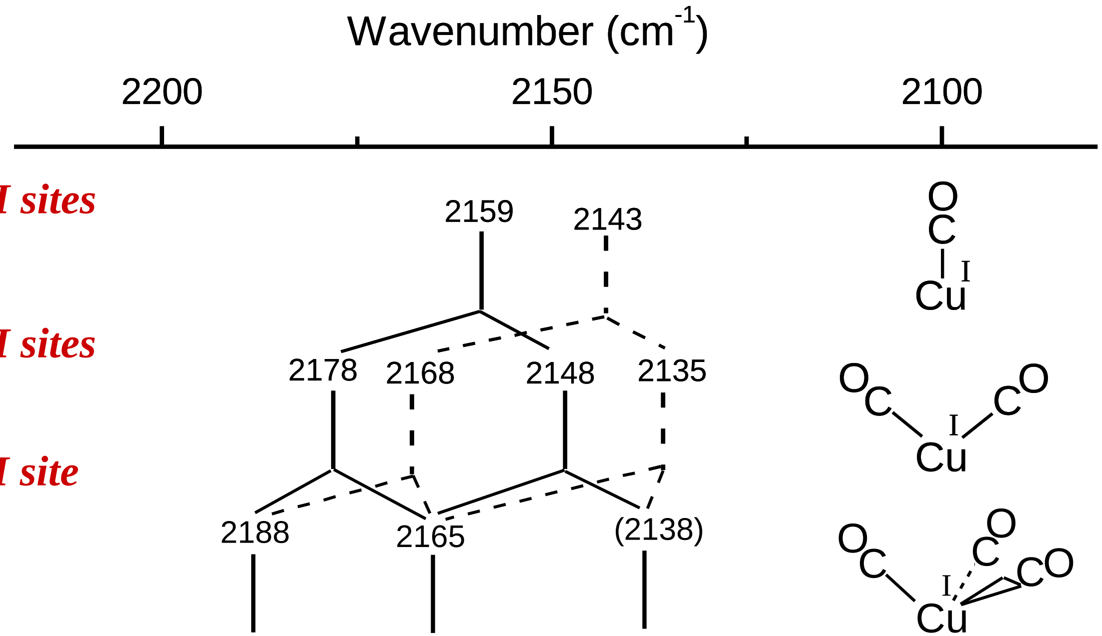
Cu+-Y: XRPD explains IR data



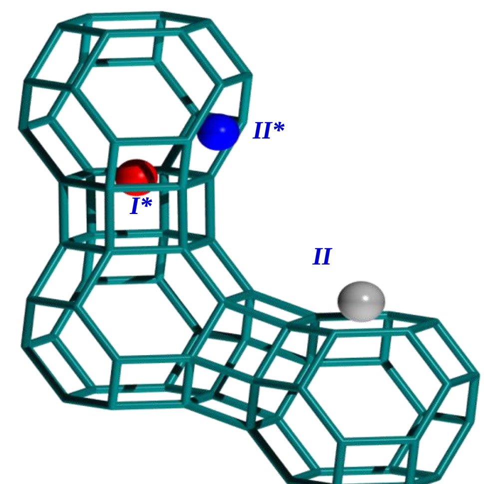
Two II sites

Two II sites

One II site

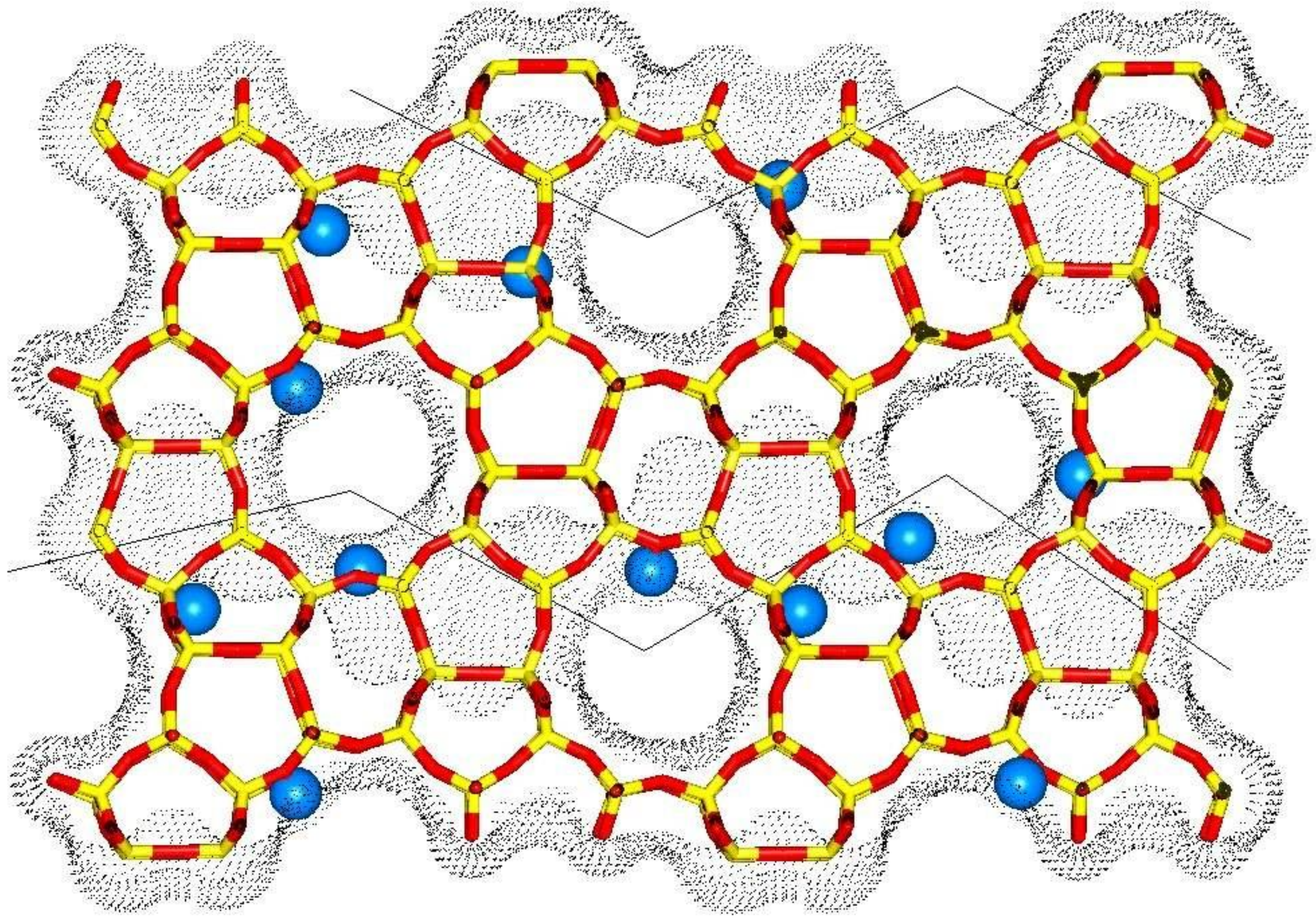


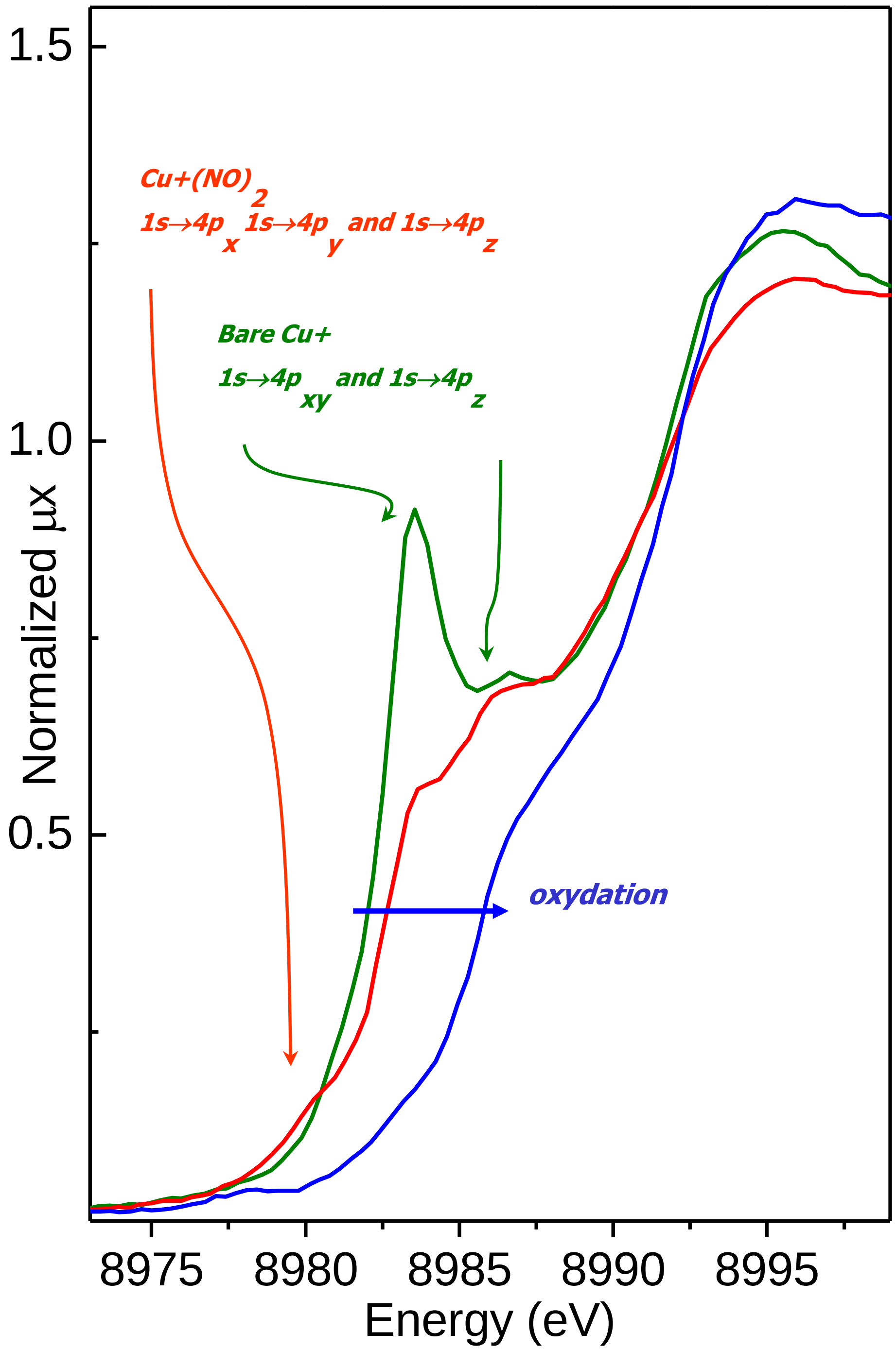
Increasing P_{CO}



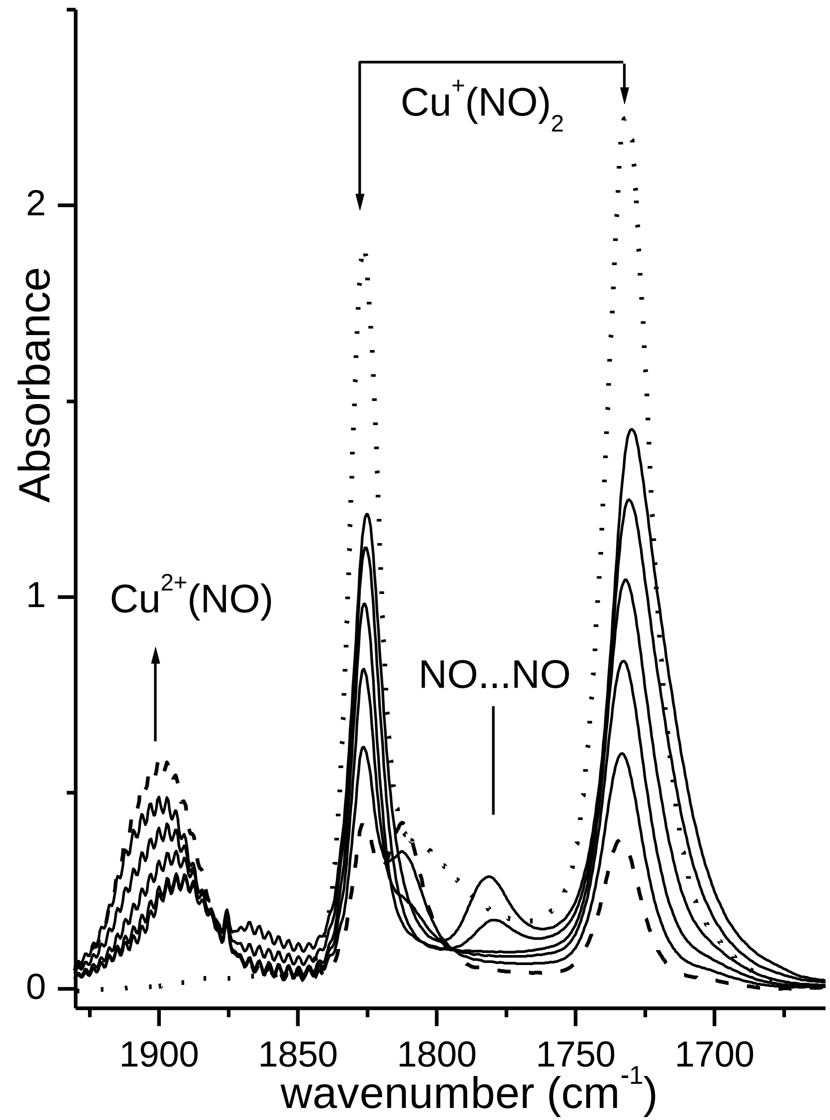
Turnes Palomino, et al., J. Phys. Chem. B, 2000, 104, 4064

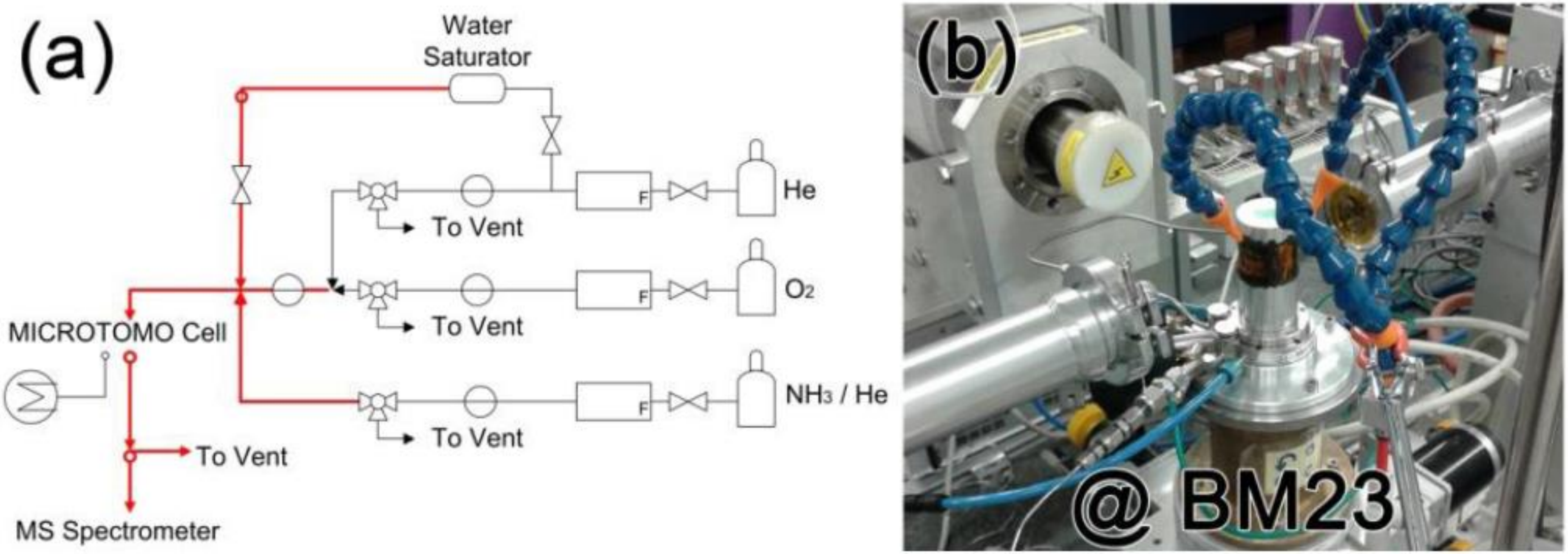
MFI





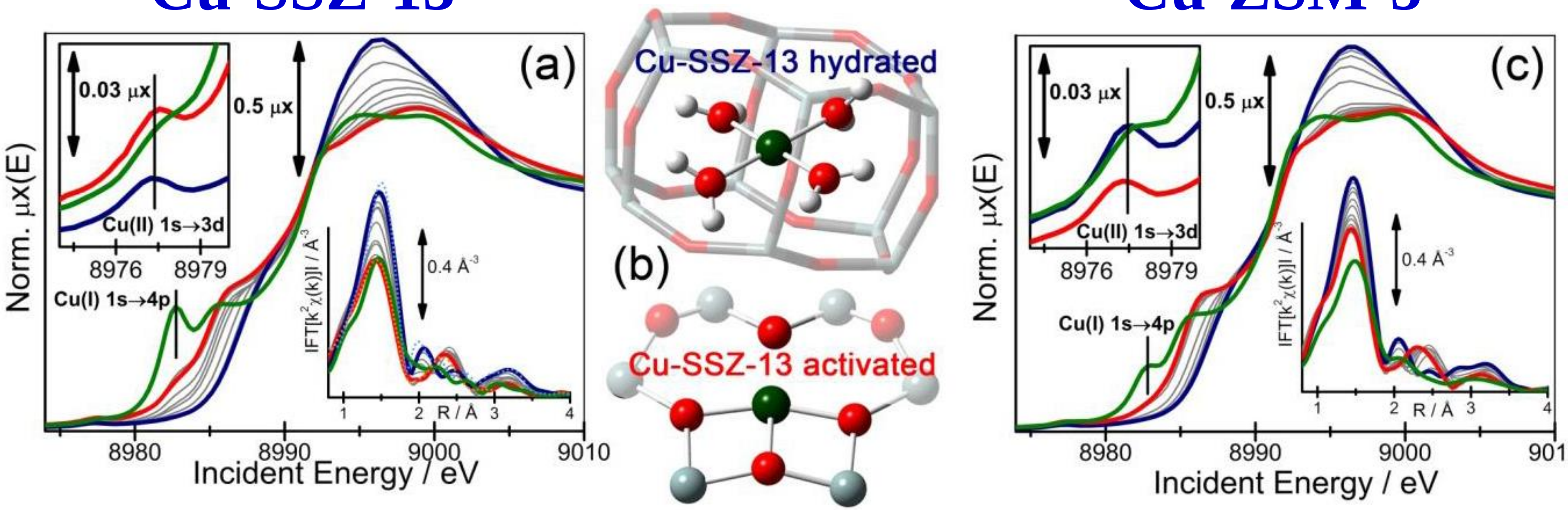
Prestipino et al., Chem. Phys. Let. 363 (2002) 389



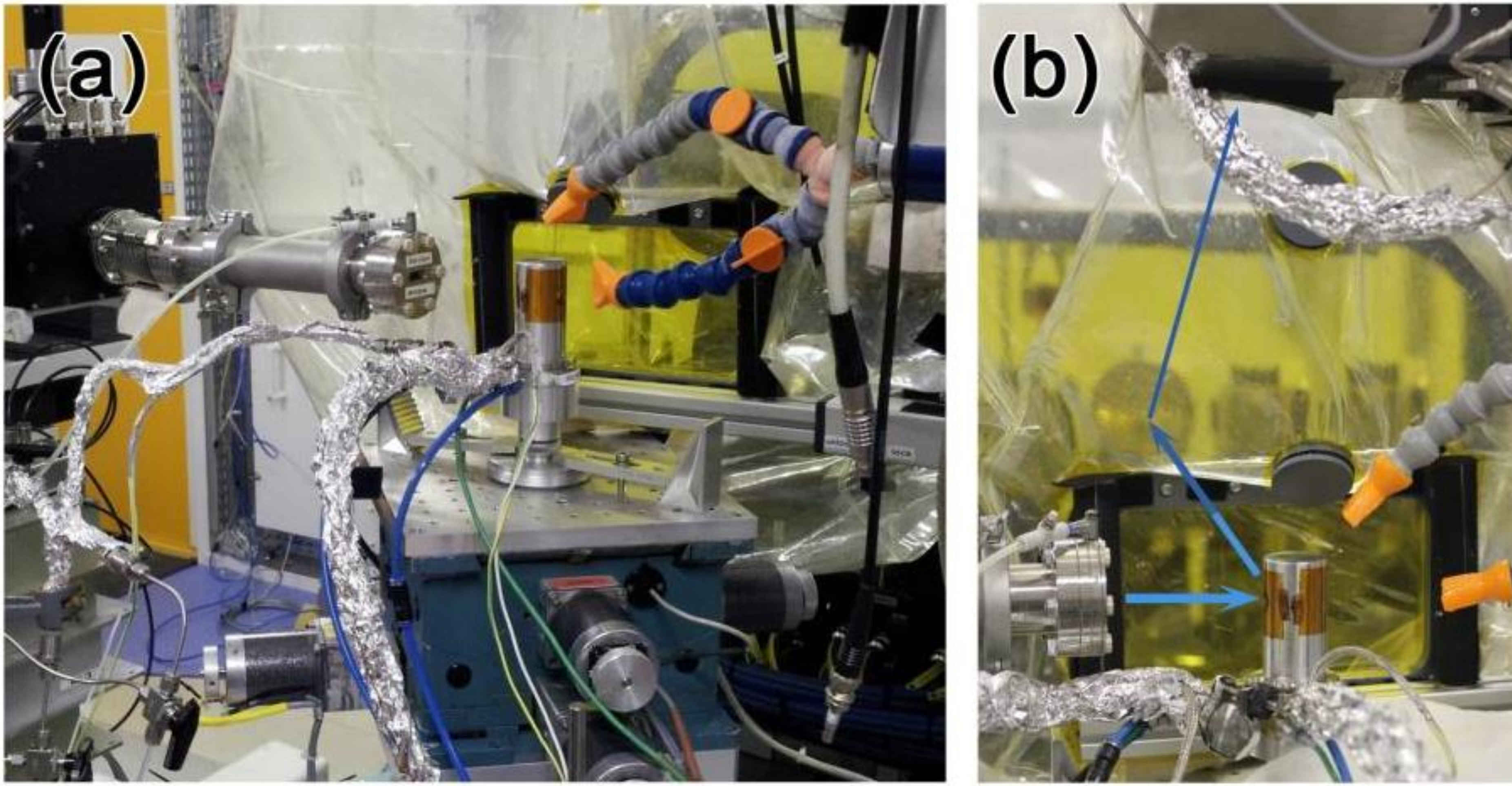


+ NH_3

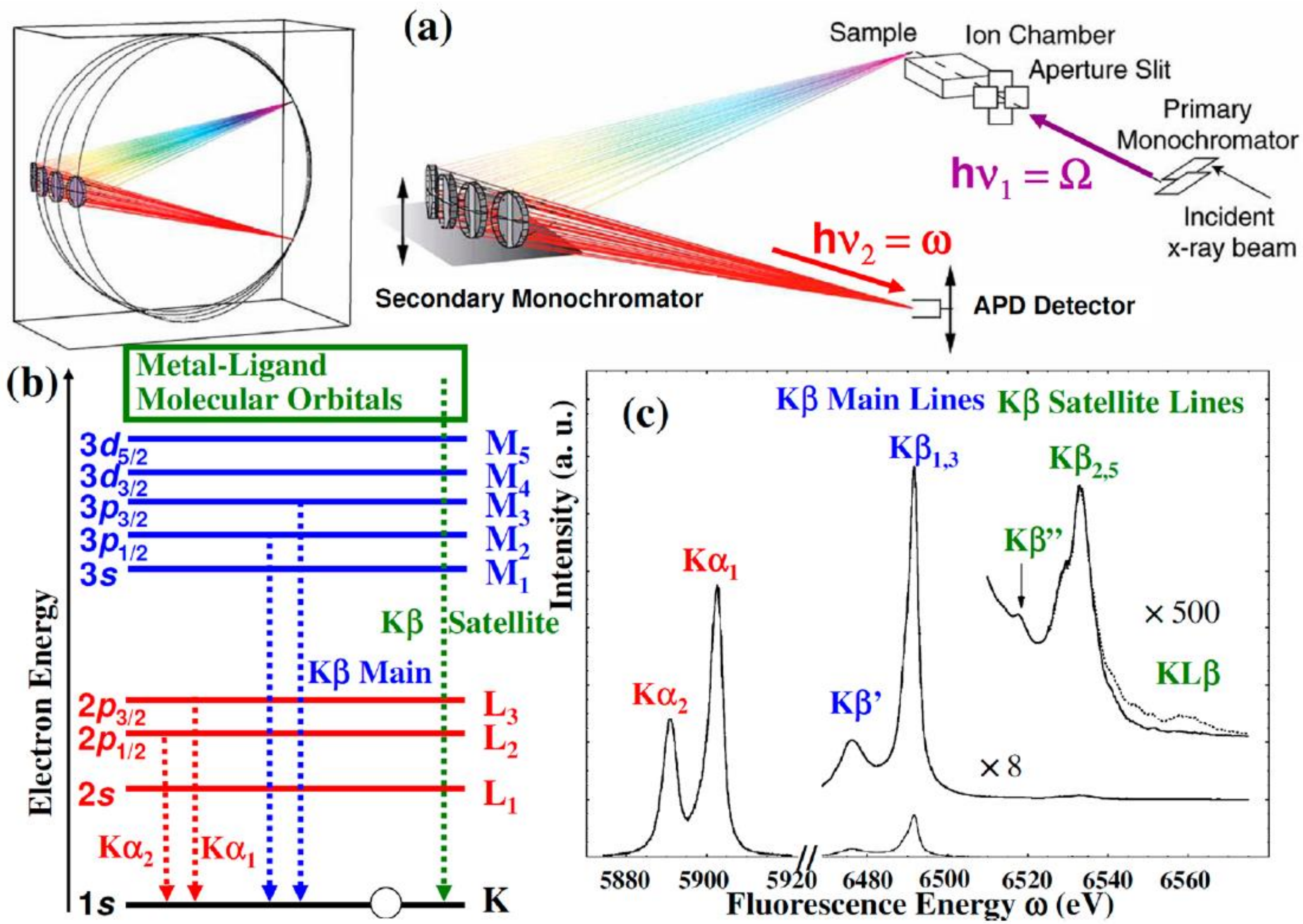
Cu-SSZ-13 **Cu-ZSM-5**

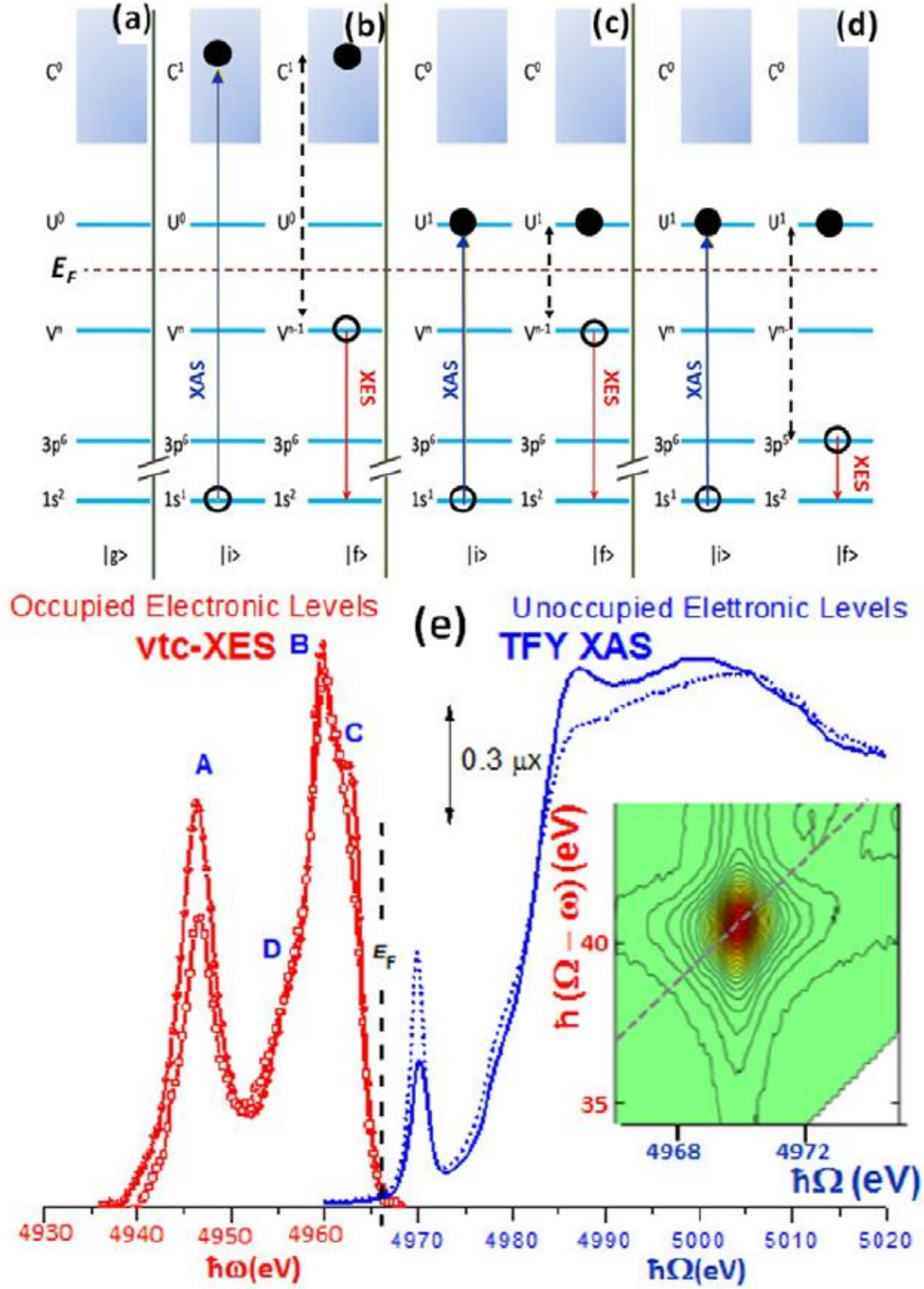


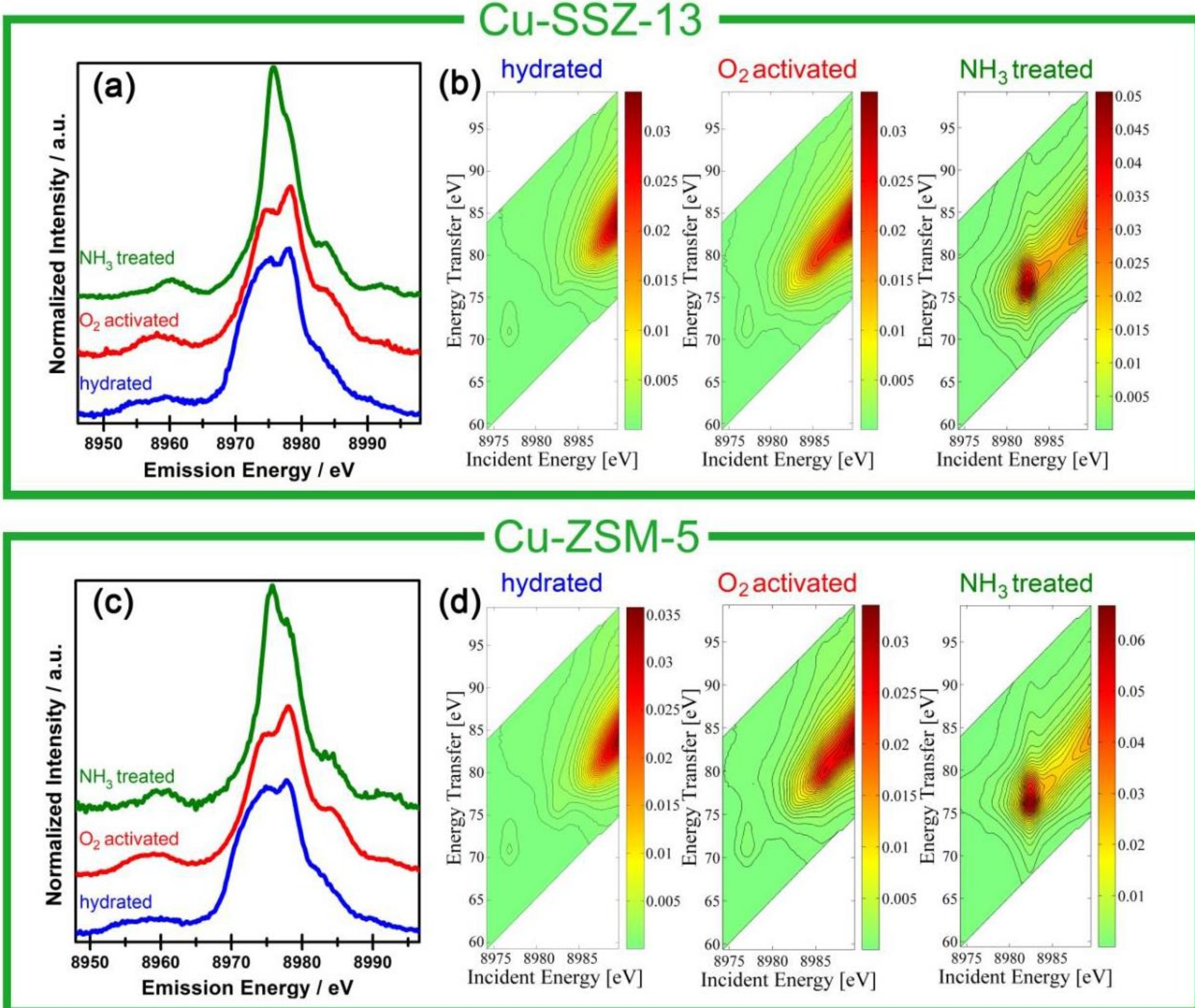
XES @ ID26



Chem. Rev. 2013, 113, 1736−1850



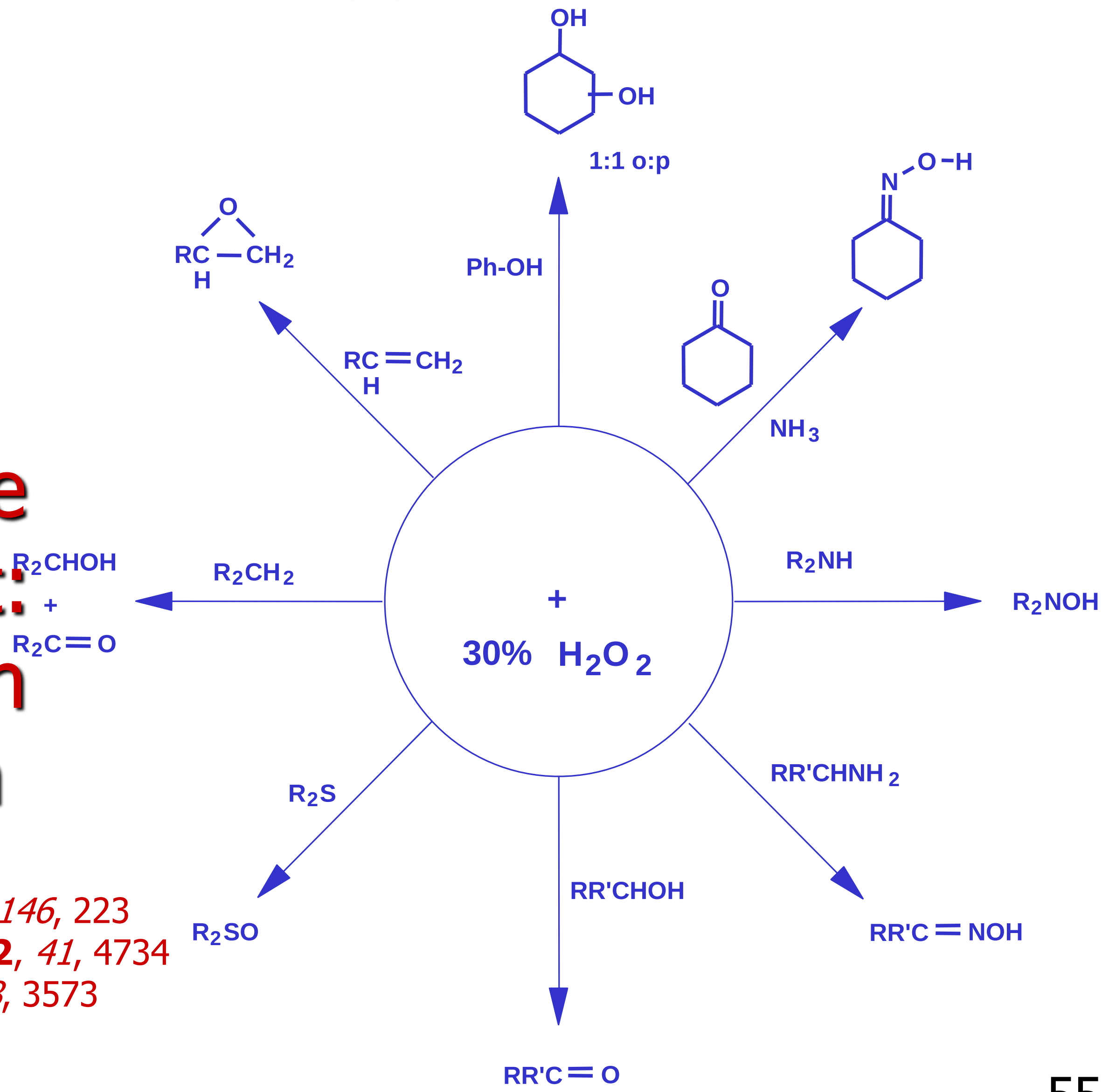

(a)
(b)
(c)
(d)
XAS
XES
|g>
|i>
|f>
Occupied Electronic Levels
Unoccupied Elettronic Levels
(e)
vtc-XES
TFY XAS
0.3 μx
ħω(eV)
ħΩ(eV)
ħ(Ω – ω)(eV)



Cu-SSZ-13
(a)
(b)
hydrated
O_2 activated
NH_3 treated
Normalized Intensity / a.u.
Emission Energy / eV
Energy Transfer [eV]
Incident Energy [eV]
Cu-ZSM-5
(c)
(d)

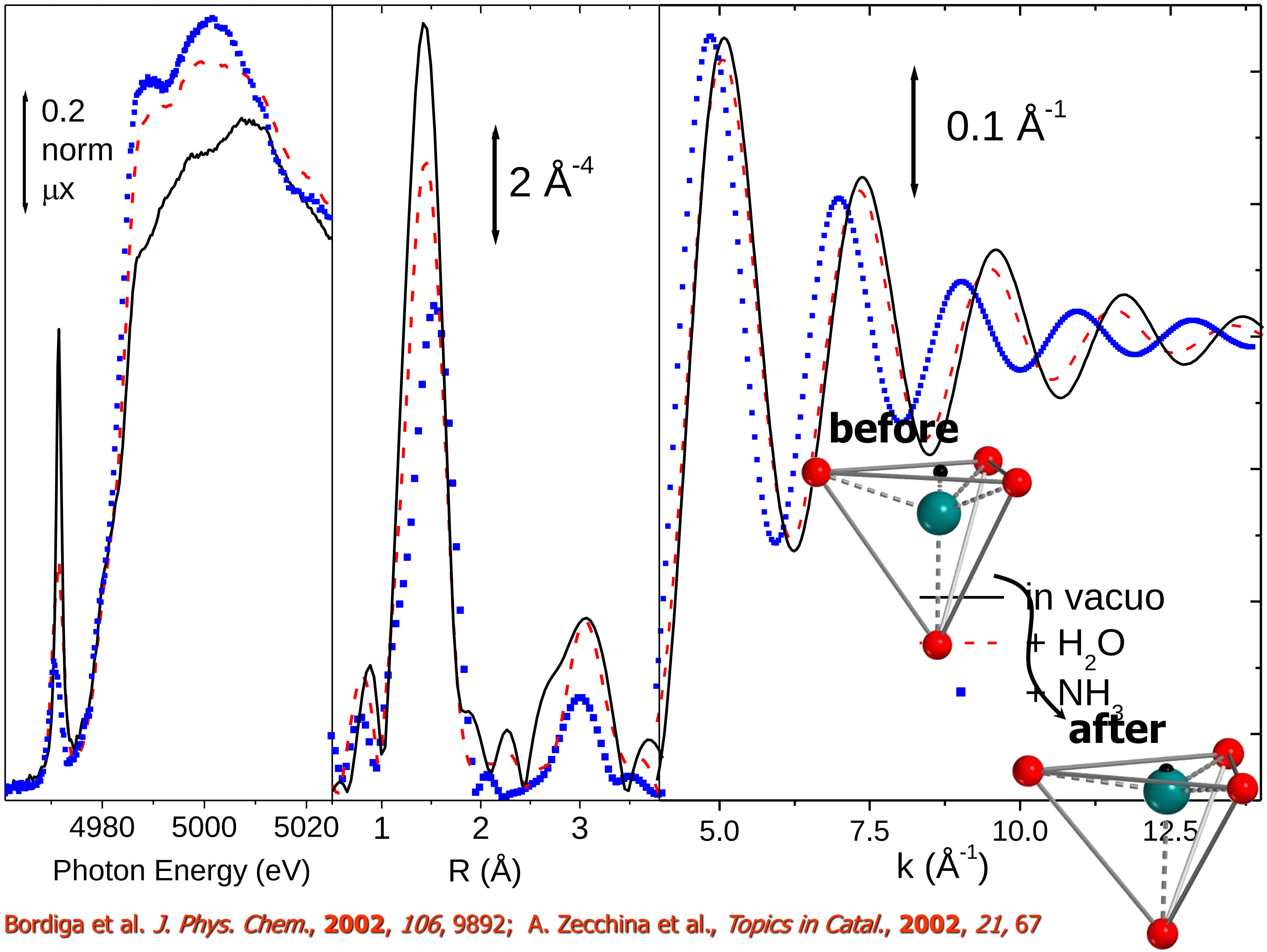
TS-1: Interest & Applications

Higly active and selective catalyst for oxidation reactions using hydrogen peroxide as oxidizing agent: Industrial plants in Europe and Japan



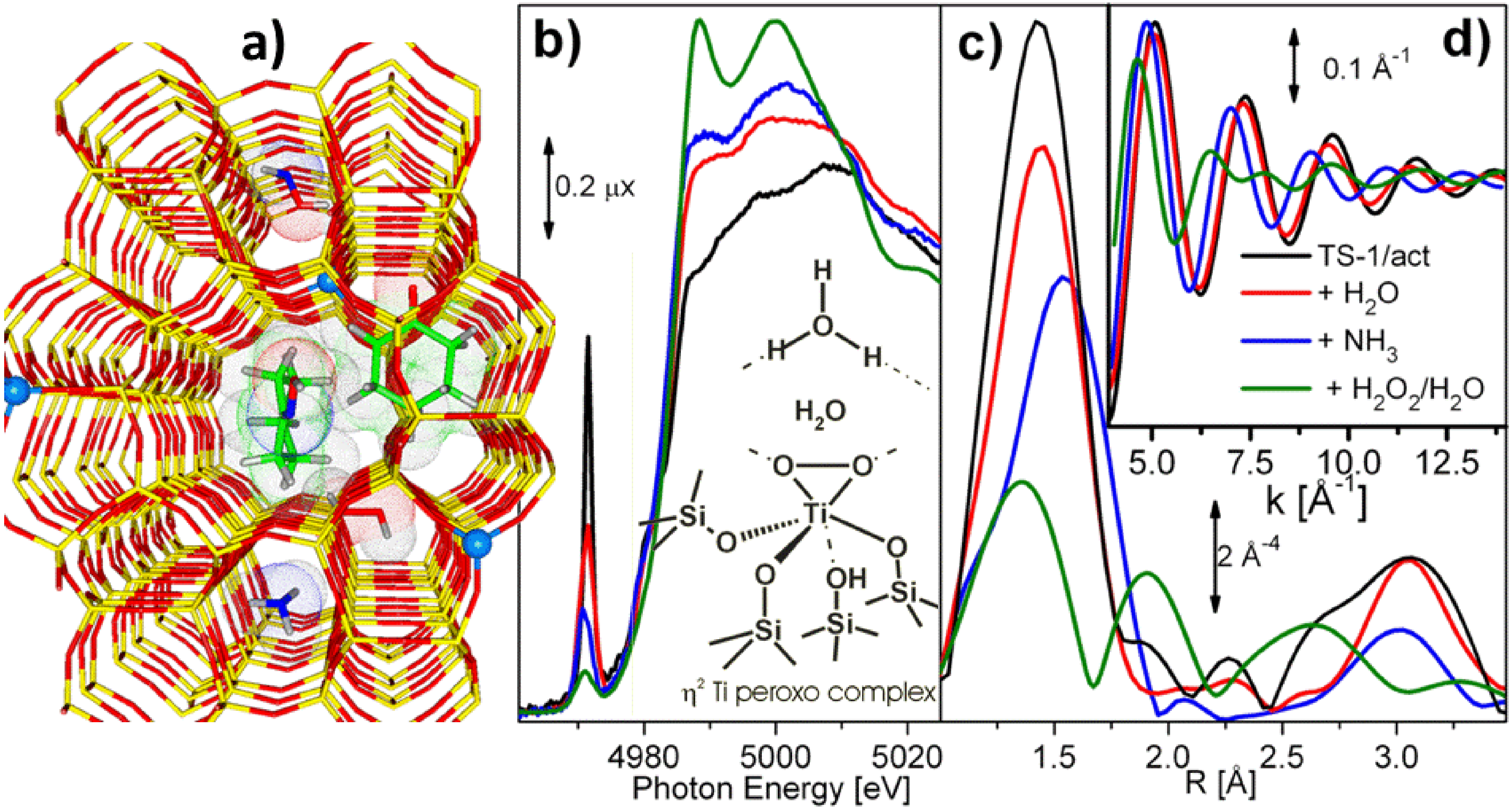
Notari, *Adv. Catal.* **1996**, *41*, 253,
Mantegazza, et al. *J. Mol. Catal. A* **1999**, *146*, 223
Bordiga et al. *Angew. Chem. Int. Ed.*, **2002**, *41*, 4734
Bonino et al., *J. Phys. Chem. B*, **2004**, *108*, 3573

TS-1: XAFS data @ ESRF BM8 GILDA



S. Bordiga et al. *J. Phys. Chem.*, **2002**, *106*, 9892; A. Zecchina et al., *Topics in Catal.*, **2002**, *21*, 67

TS-1: XAFS data @ ESRF BM8 GILDA

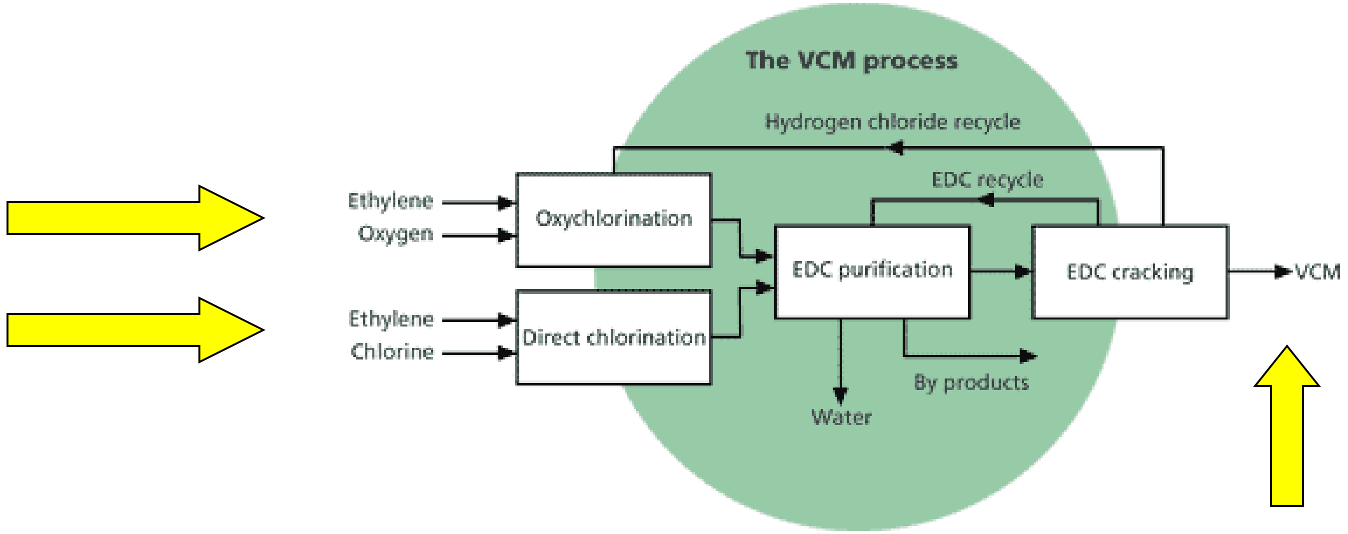


Zecchina et al., *Topics in Catal.*, **2002**, *21*, 67; F. Bonino, et al. *J. Phys. Chem. B*, **2004**, *108*, 3573
Prestipino et al. *ChemPhysChem.*, **2004**, *5*, 1799

The PVC $[-CH_2-CHCl-]_n$

- A wide use polymeric material
- It used in electronic, building,farmaceutic, and in several different kind of applications

The chemistry of PVC



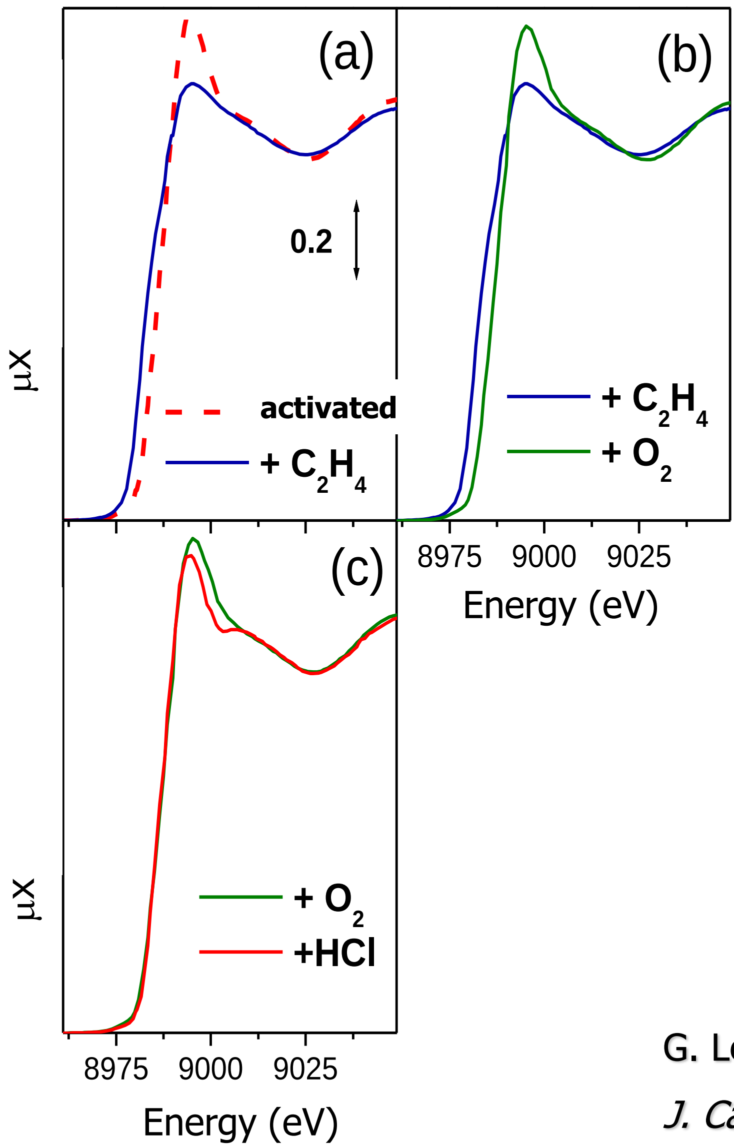
The oxychlorination reaction ($CuCl_2$) :

$$C_2H_4 + 2HCl + \frac{1}{2} O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

The cracking of 1,2-dichloroethane:

$$C_2H_4Cl_2 \rightarrow CH_2{=}CHCl + HCl$$

Understanding the basic reactions



Catalyst: $CuCl_2/\gamma\text{-}Al_2O_3$

Evolution of the XANES spectra after interaction with reactants

a) Reduction of $CuCl_2$ to CuCl by C_2H_4 :

$$2CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 2CuCl$$

b) Re-oxidation of CuCl by oxygen:

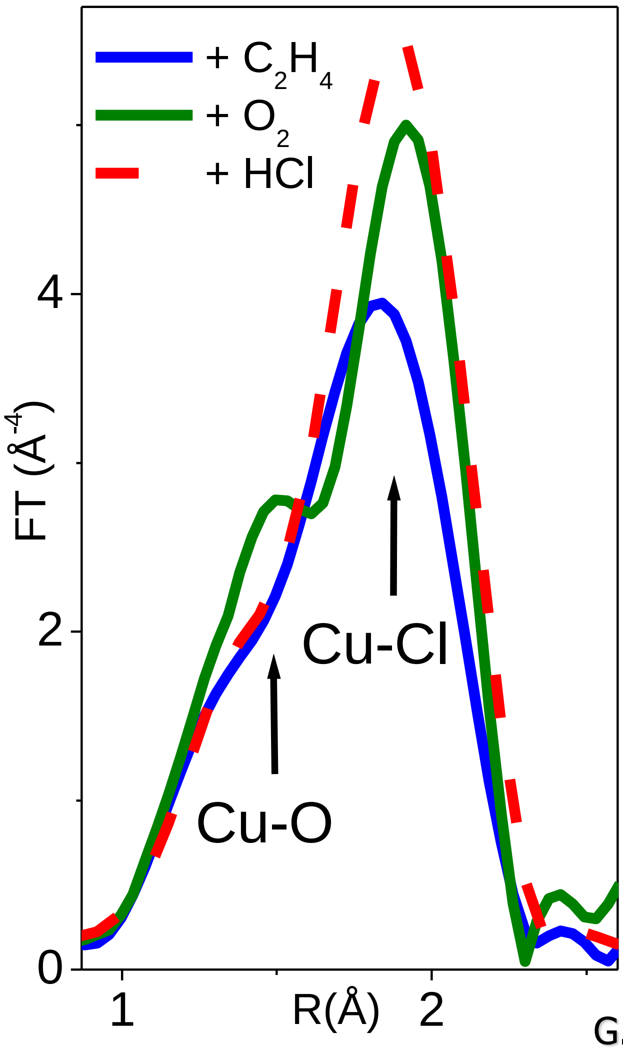
$$2CuCl + ½\, O_2 \rightarrow Cu_2OCl_2$$

c) Closure of the catalytic cycle by re-chlorination by HCl yielding $CuCl_2$:

$$Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

G. Leofanti et al. *J. Catal.,* **189** (2000) 91; *J. Catal.,* **189** (2000) 105; *J. Catal.,* **202** (2001) 279; *J. Catal.,* **205** (2002) 275

Understanding the basic reactions



Catalyst: $CuCl_2/\gamma\text{-}Al_2O_3$

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a) Reduction of $CuCl_2$ to CuCl by C_2H_4 :

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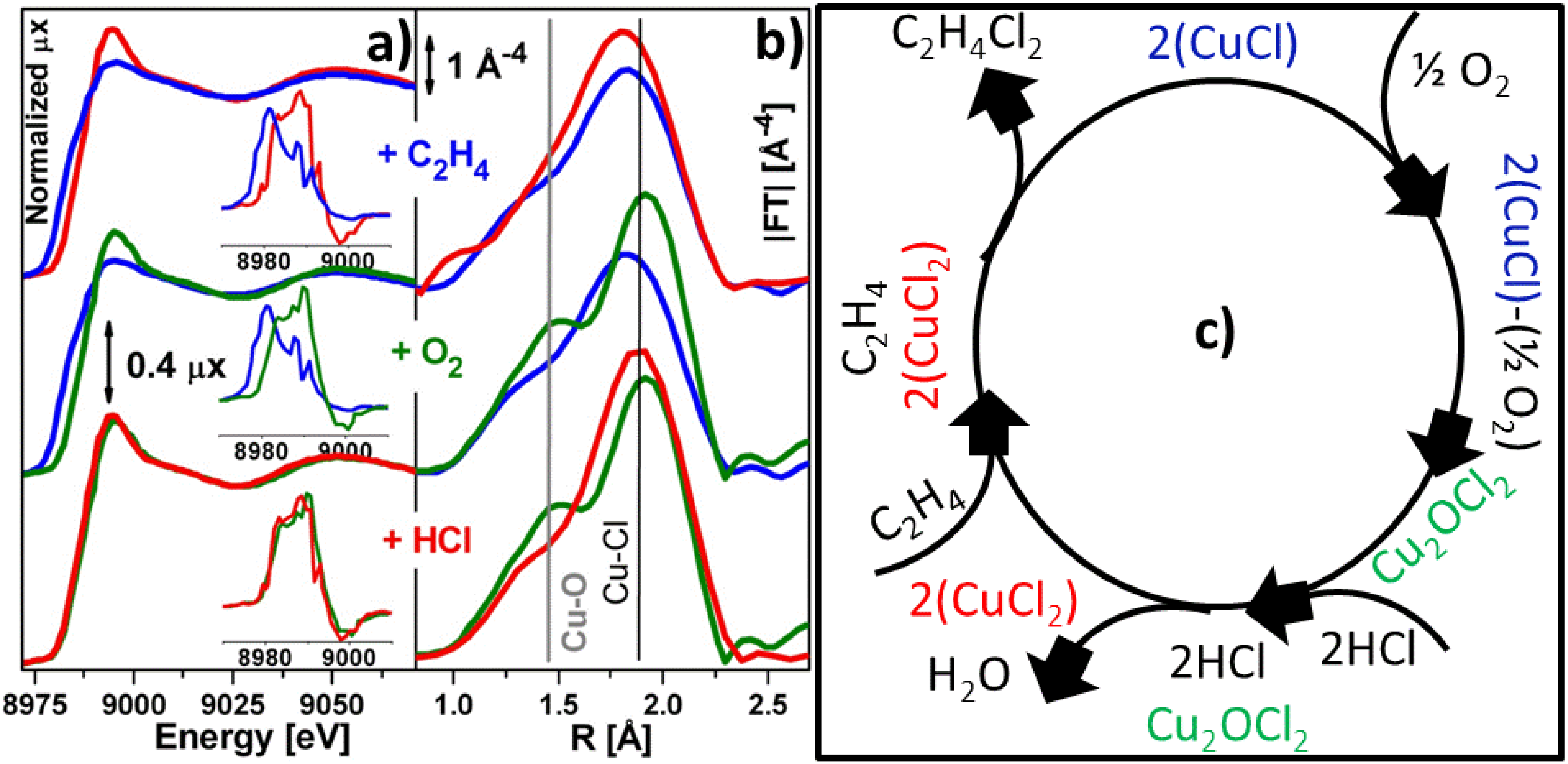
b) Re-oxidation of CuCl by oxygen:

$$2CuCl + \tfrac{1}{2} O_2 \rightarrow Cu_2OCl_2$$

c) Closure of the catalytic cycle by re-chlorination by HCl yielding $CuCl_2$:

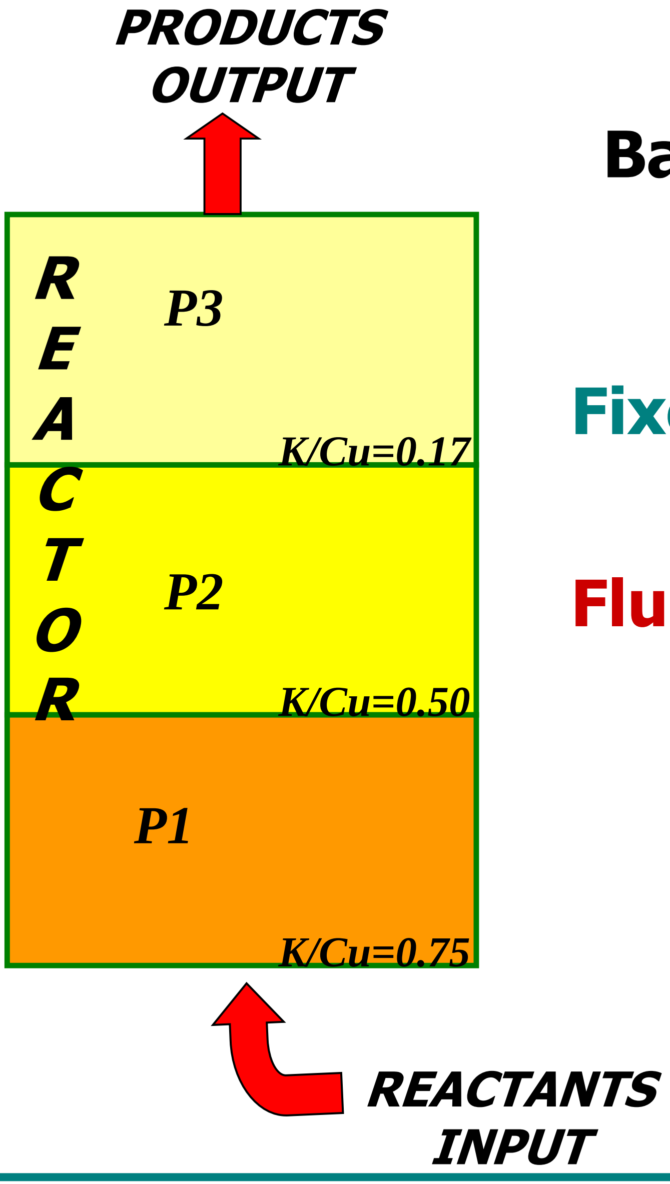
$$Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

G. Leofanti et al. *J. Catal.*, **189** (2000) 91; *J. Catal.*, **189** (2000) 105; *J. Catal.*, **202** (2001) 279; *J. Catal.*, **205** (2002) 275



a)
Normalized μx
+ C_2H_4
+ O_2
+ HCl
0.4 μx
8980
9000
8975
9000
9025
9050
Energy [eV]
b)
1 $Å^{-4}$
|FT| [$Å^{-4}$]
Cu-O
Cu-Cl
1.0
1.5
2.0
2.5
R [Å]
c)
$C_2H_4Cl_2$
2(CuCl)
½ O_2
2(CuCl)-(½ O_2)
Cu_2OCl_2
2HCl
2HCl
Cu_2OCl_2
H_2O
2($CuCl_2$)
C_2H_4
C_2H_4
2($CuCl_2$)

The use of additives in the industrial catalysts



Base catalyst: $CuCl_2/\gamma\text{-}Al_2O_3$

Fixed bed reactors → **Potassium**

Fluid bed reactors → **Magnesium**

Other additives : Li, Cs, Ce, La

GOALS and TECHNIQUES

First goal:

The study of the effects of

additives

and of their concentration

Second goal:

Determination of the

rate determining step

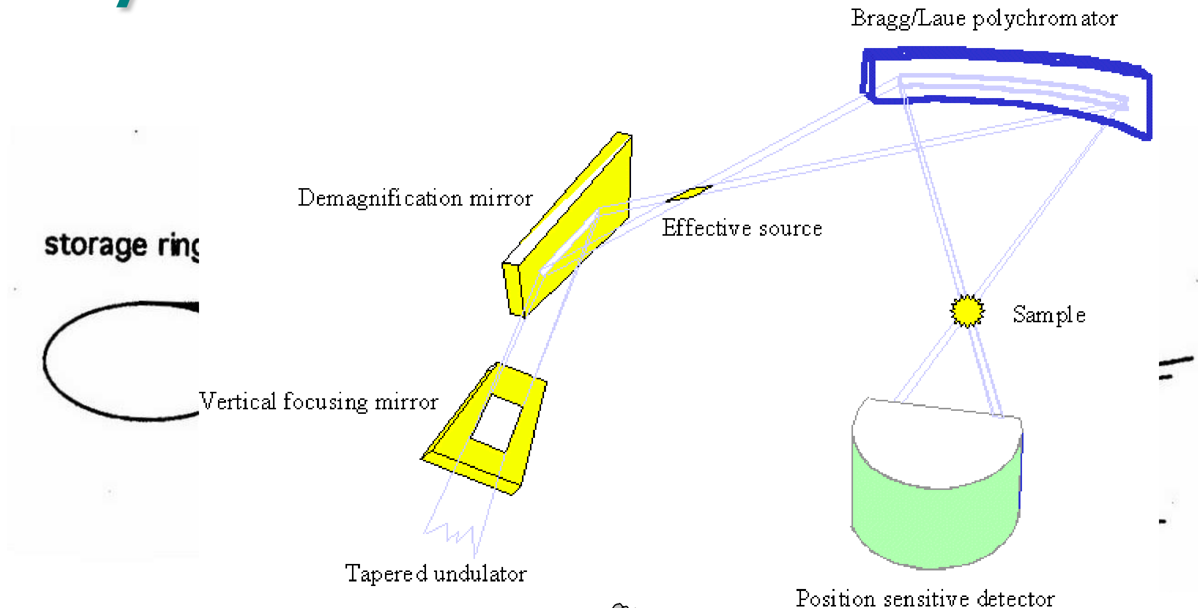
Of the ethylene oxychlorination reaction

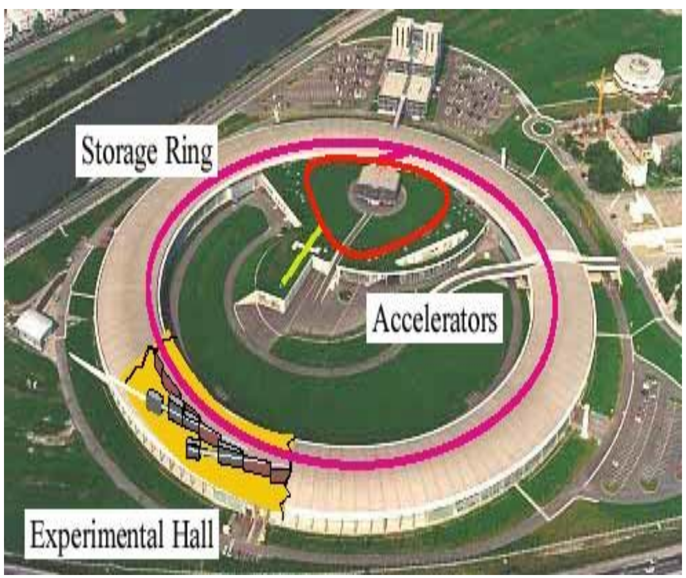
dispersive XAS

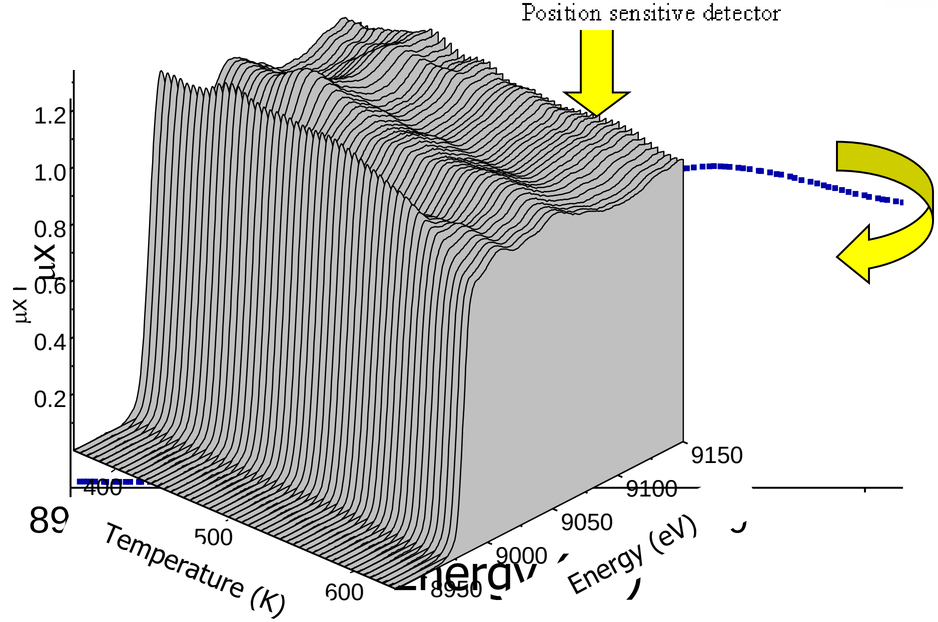
Different X-ray absorption techniques

Dispersive
Geometry

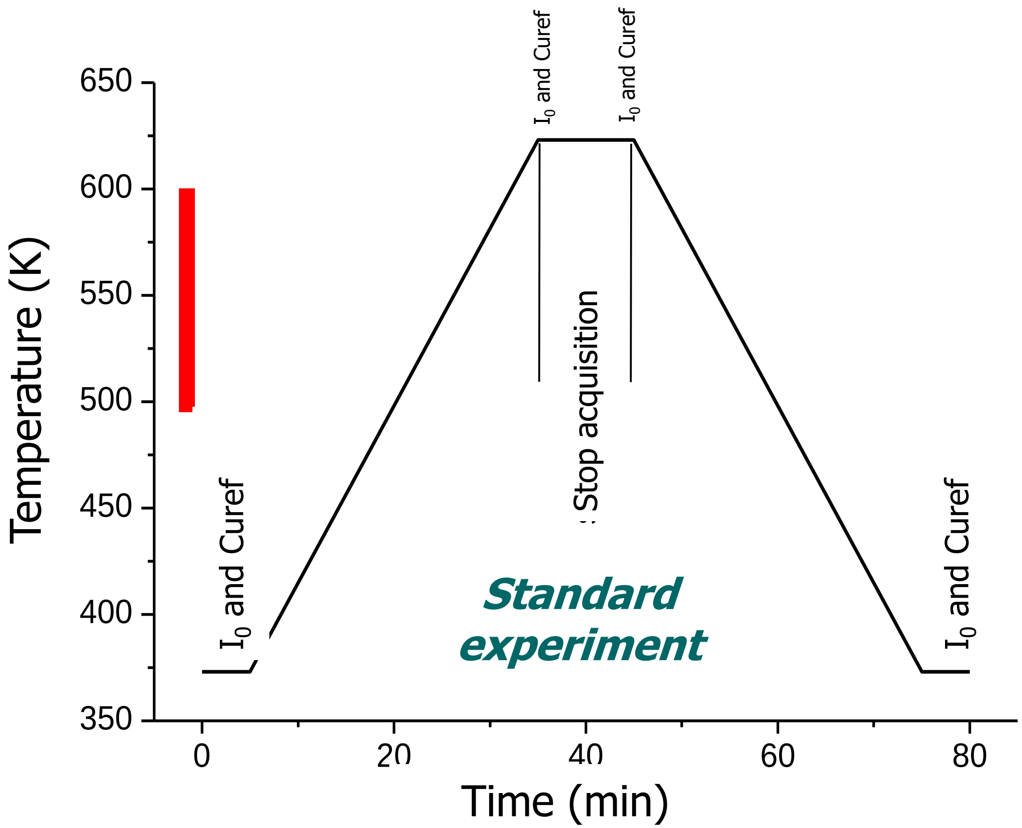
Classical
monochromatic
geometry







Experiment description @ ID24

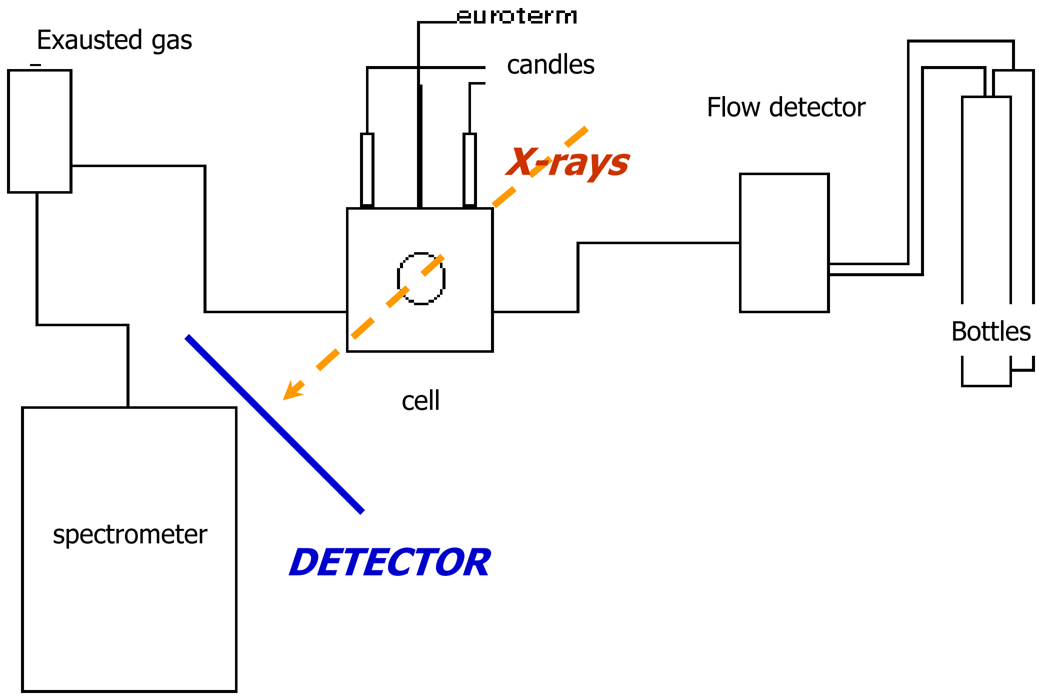


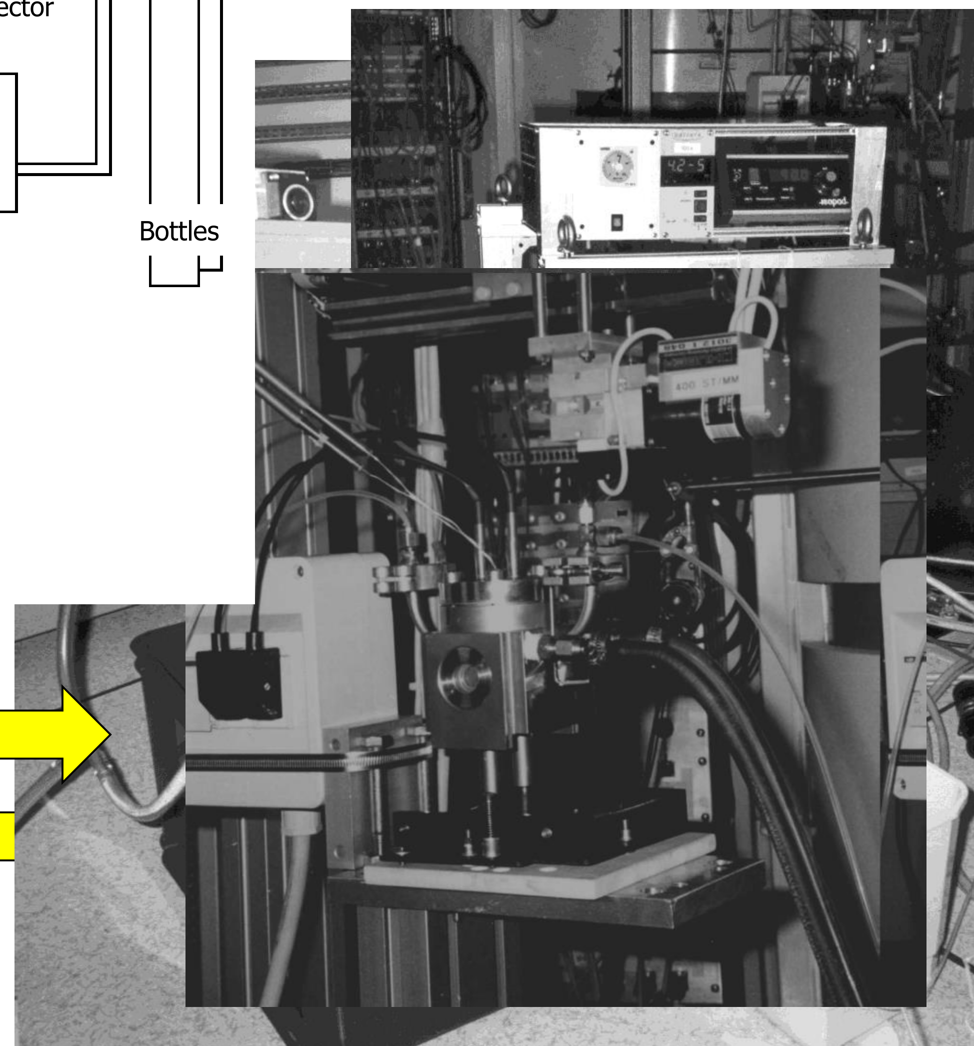
Composition of the reactant flux:

N_2	13cc/min.
C_2H_4	100cc/min.
HCl	36.1cc/min.
O_2	7.6cc/min.

- Ramp up from 373 to 623 K
- Isotherm at 623 K
- Ramp down from 623 back to 373 K

Description of the experimental set-up @ ID24





Mass spectrometer

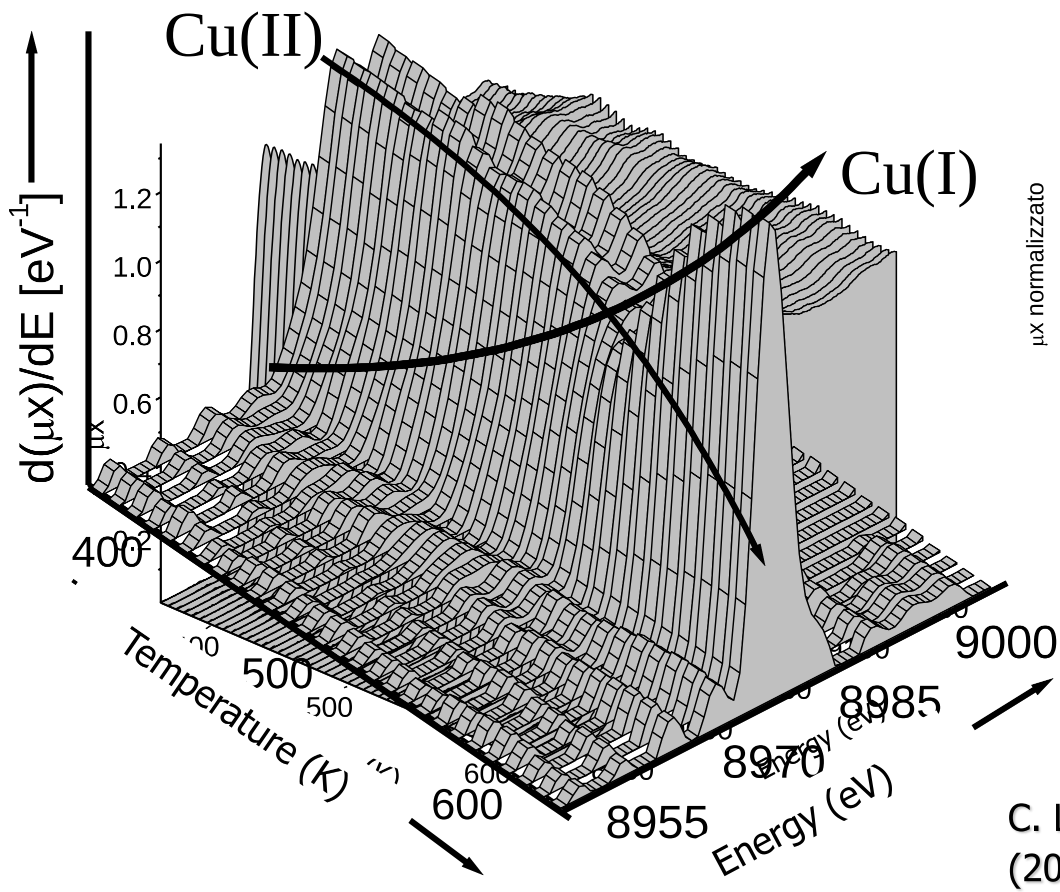
Zoom on the cell

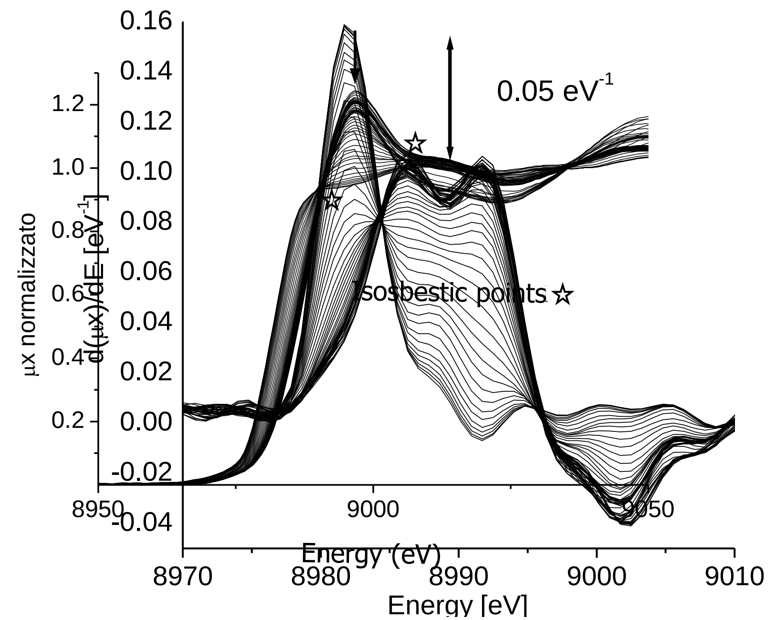
Exhaust gases elimination

XAFS cell and positioning motors

Base catalyst $CuCl_2/\gamma\text{-}Al_2O_3$

Ramp up: Cu(II) → Cu(I)





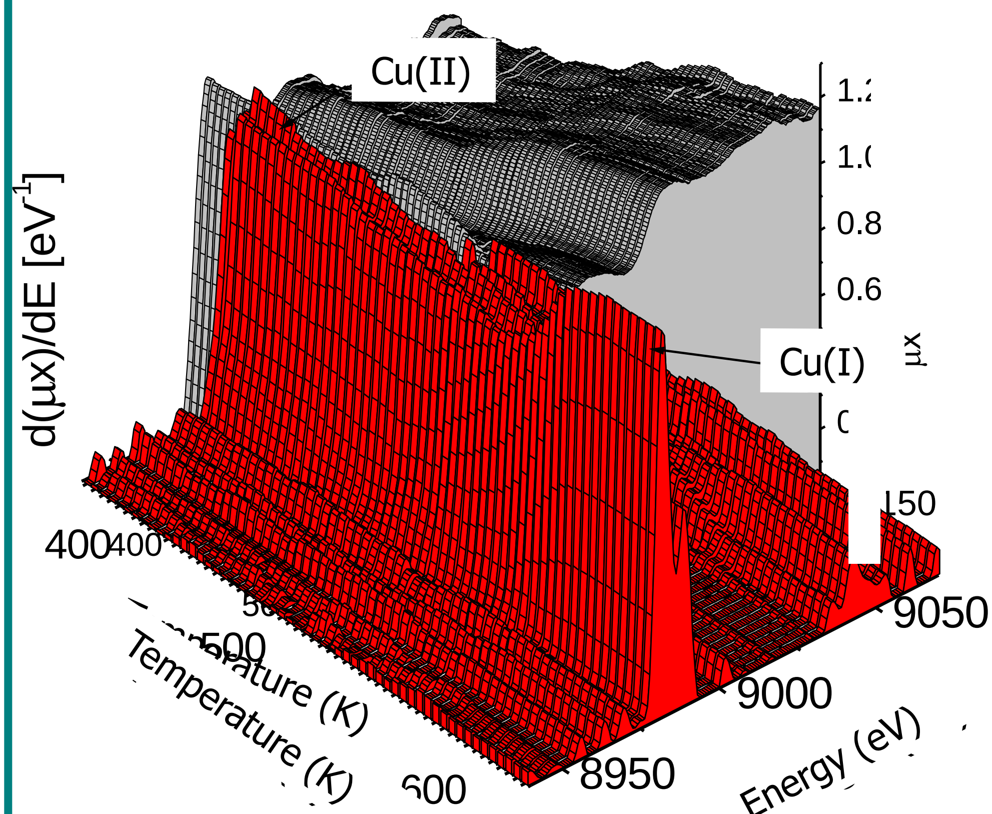
XANES spectra

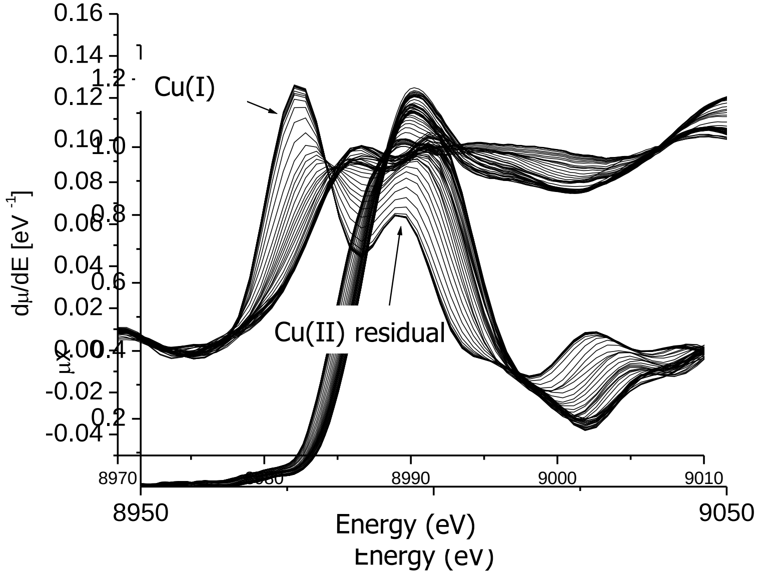
First derivative spectra

C. Lamberti, et al. *Angew. Chem. Int. Ed.,* **41** (2002) 2341-2344

K-$CuCl_2$/γ-Al_2O_3 catalyst

Ramp up: Cu(II) → Cu(II)+Cu(I)



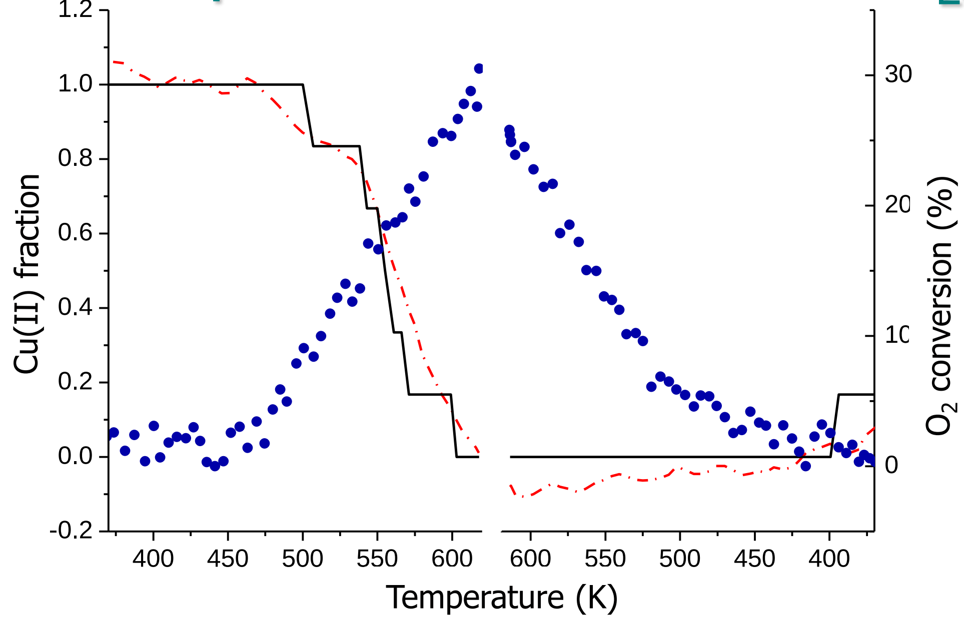


XANES spectra

First derivative spectra

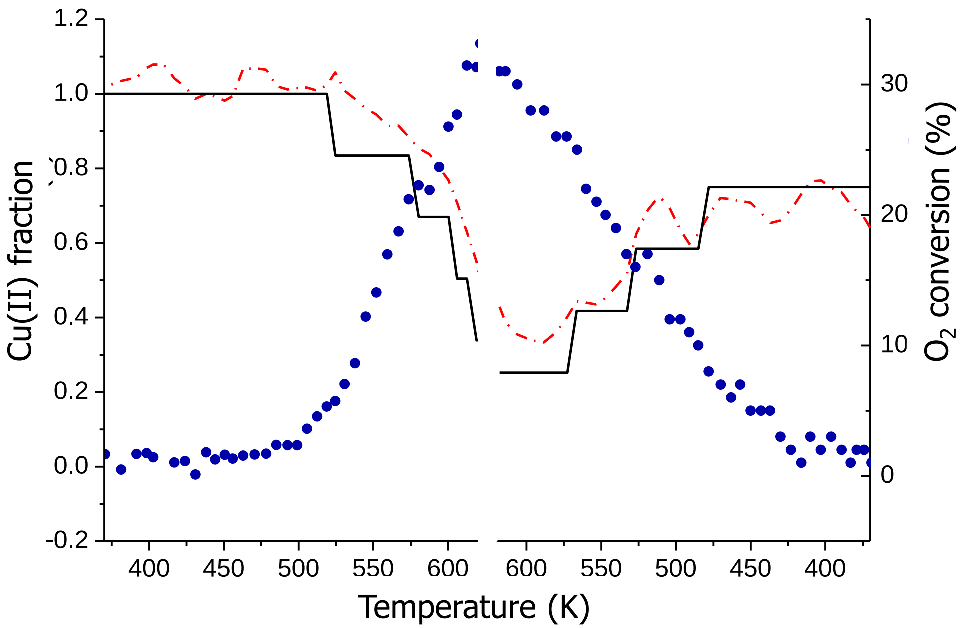
C. Lamberti, et al. *Angew. Chem. Int. Ed.,* **41** (2002) 2341-2344

Comparison between K-$CuCl_2/\gamma$-Al_2O_3 and $CuCl_2/\gamma$-Al_2O_3



$CuCl_2/\gamma$-Al_2O_3

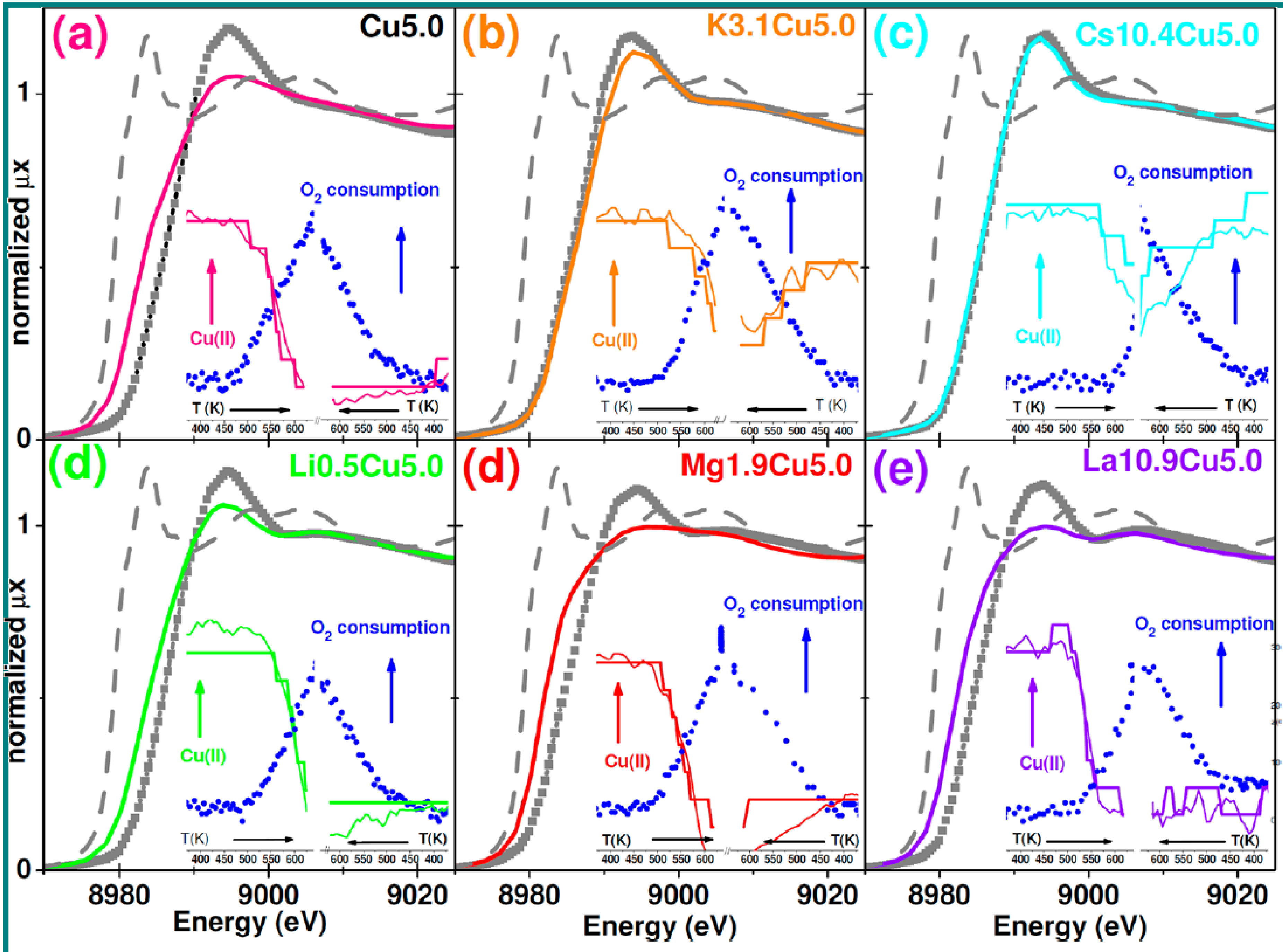
- Totally reduced at the end of the ramp up
- Not re-oxidized during the ramp down
- The activity of the catalysts starts with the reduction, within our accurancy (±10 K)



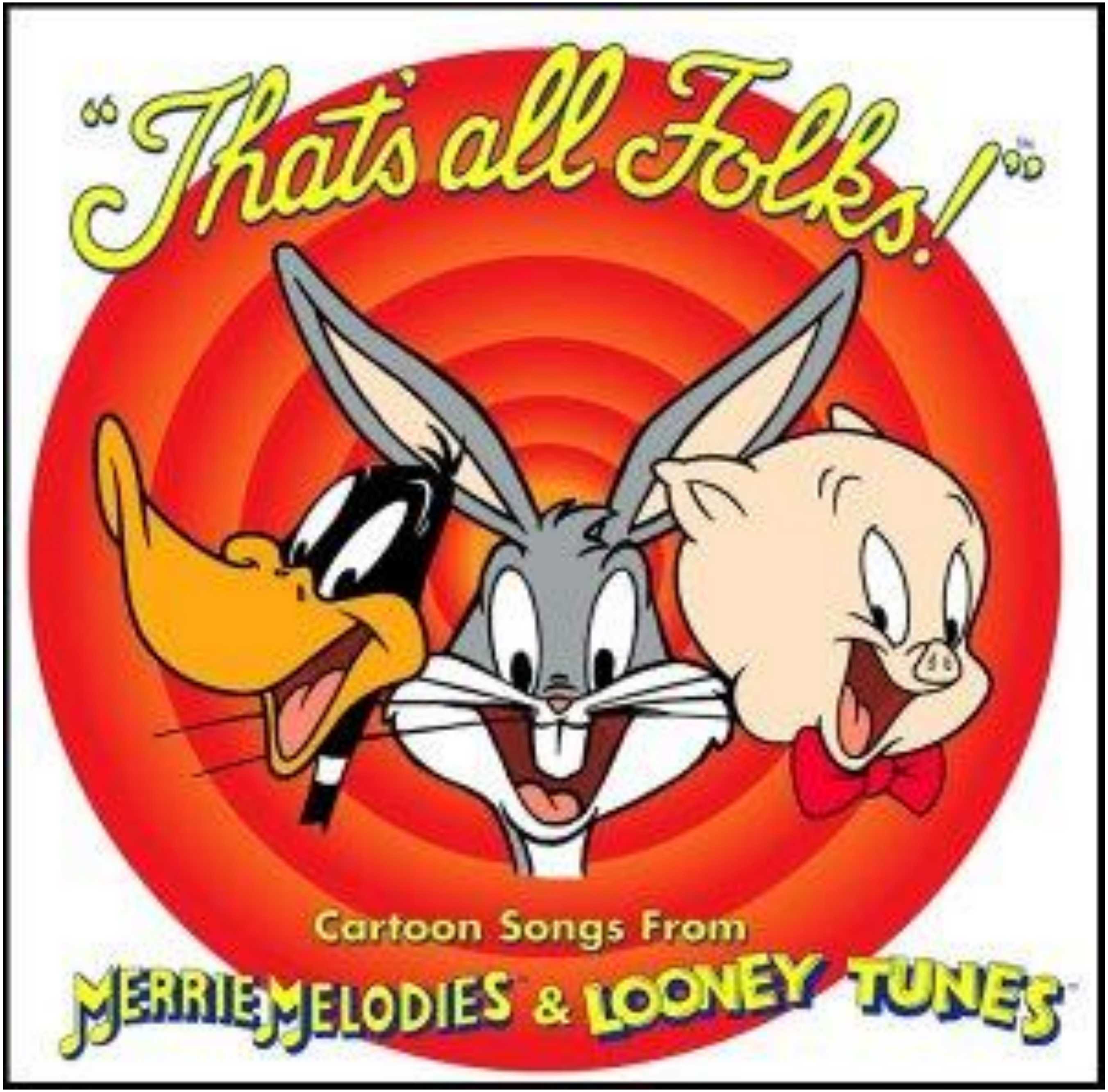
K-$CuCl_2/\gamma$-Al_2O_3

- Partially reduced at the end of the ramp up
- Re-oxidized during the ramp down
- The activity starts before the reduction

C. Lamberti, et al. *Angew. Chem. Int. Ed.*, **41** (2002) 2341-2344



(a)
Cu5.0
(b)
K3.1Cu5.0
(c)
Cs10.4Cu5.0
(d)
Li0.5Cu5.0
(d)
Mg1.9Cu5.0
(e)
La10.9Cu5.0
normalized μx
O2 consumption
Cu(II)
T (K)
400 450 500 550 600
600 550 500 450 400
0
1
8980
9000
9020
Energy (eV)


"That's all Folks!"
Cartoon Songs From
MERRIE MELODIES & LOONEY TUNES