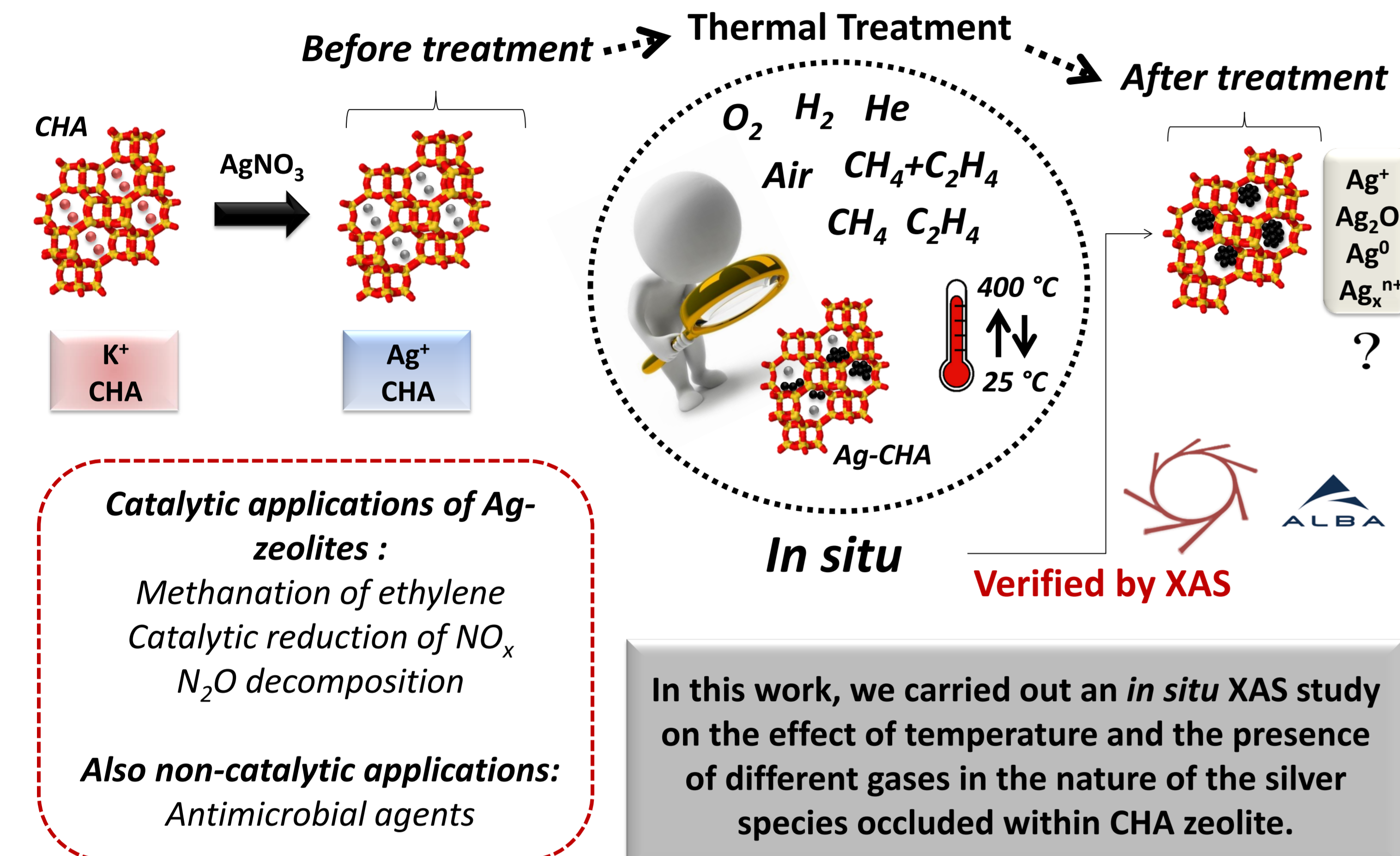


Background

Why study silver zeolites by XAS?

The reversible oxidation-reduction of silver in zeolites provides an excellent model system for studying the mechanism of formation of noble metal clusters within zeolite channels and cavities.^[1] The zeolite cages provide a practical means of preventing the cluster cohesion, because small metal clusters have a strong tendency to form larger particles ($d > 10$ nm) driven by surface energy minimization.^[2] It would be expected that the zeolite pore topology (LTA, FAU, CHA, RHO, etc.) could drive the clustering of Ag species during thermal treatment of Ag-zeolites in a different way. XAS analysis could shed light on silver oxidation state and local structural information of their aggregation from isolated silver cations into clusters under different controlled *in situ* thermal conditions. The low stability and lack of ordering of the clusters located in Ag-zeolites difficult the characterization by other techniques, highlighting the importance of XAS in this study.



Experimental

CHA synthesis:

Y zeolite (CBV 500)	KOH	H ₂ O
5.05 g	2.67 g	42.6 g

Yield: 4.9 g

- Gel formation for 30 minutes
- Autoclave – Static – 100 °C – 4 days
- Filtered, washed with H₂O and dried for 24 h at 100 °C

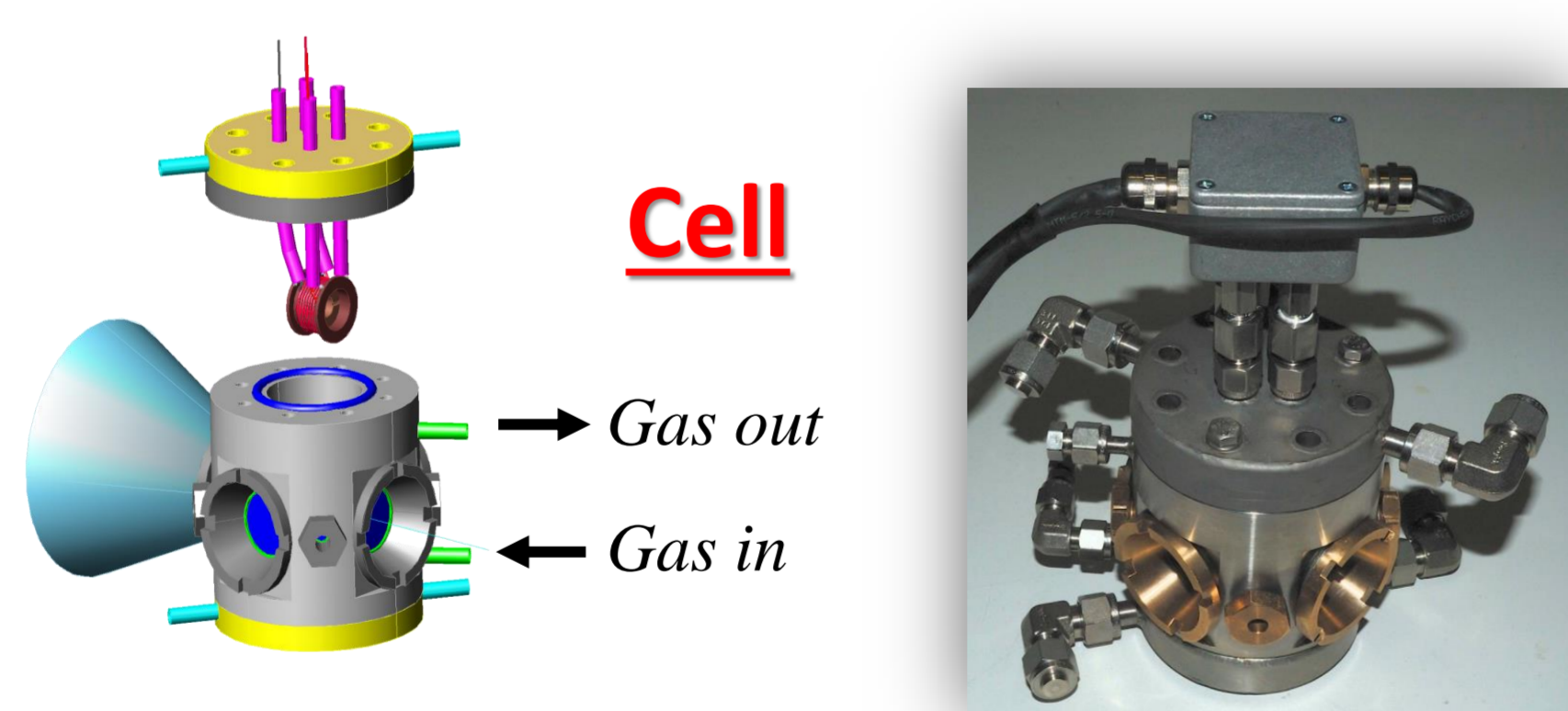
Ag-CHA preparation (fully exchanged):

1 g CHA + 0.9 g AgNO₃ – 16 hours – RT
(Covered with Al foil to avoid contact with light) → Dried for 12 h at 100 °C

In situ XAS study:

O₂, He, H₂
Gas flow: 100 mL/min
Different temperatures (RT – 400 °C)
Ambient pressure

Ag K-Edge (25514 eV)
Transmission mode
BL22 CLÆSS
ALBA synchrotron – Spain



XAS data analysis:

The spectra were normalized and treated with the Athena software.^[3] EXAFS data analysis was performed using the Artemis software.^[3] Phase and amplitudes have been calculated by FEFF6 code^[4] and successfully checked with Ag metal foil.

Preliminary results – Ag-CHA as-prepared

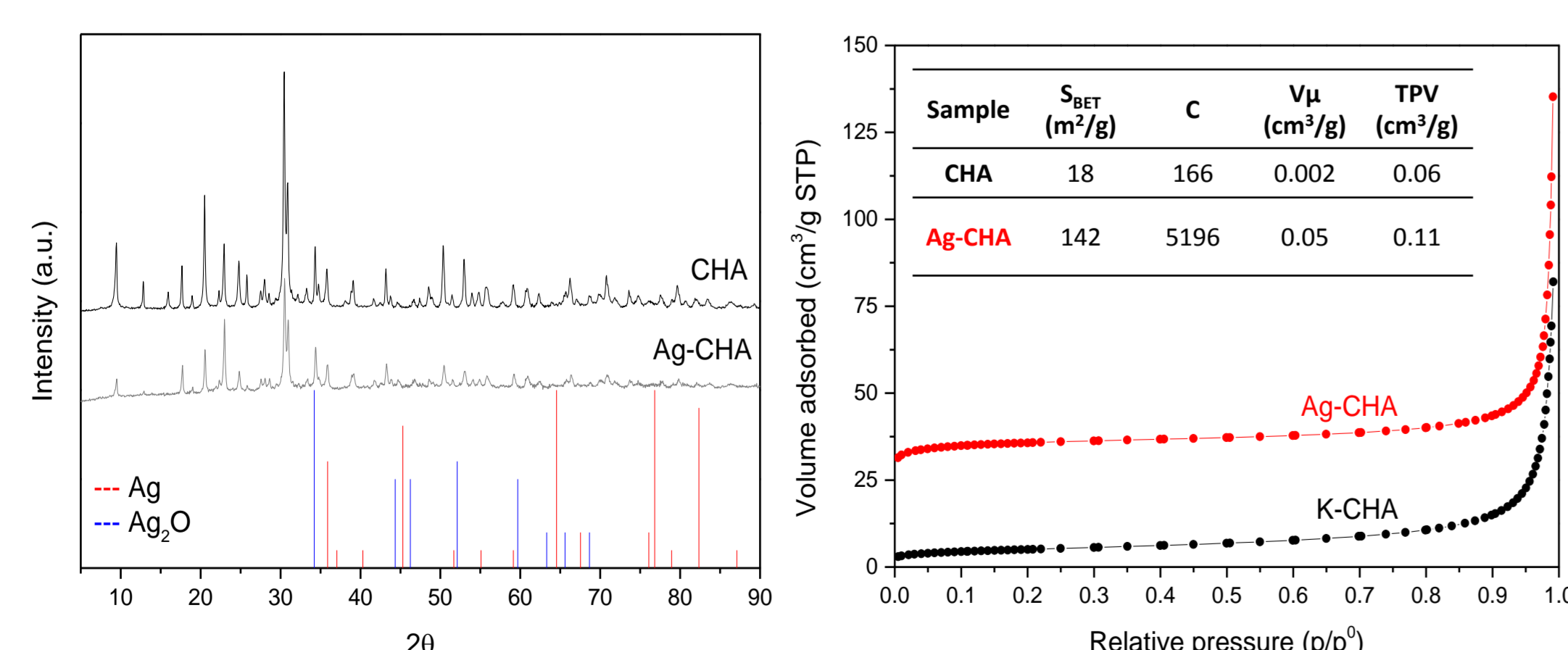


Fig. 1. XRD (left) and N₂ adsorption isotherms (right) of CHA and Ag-CHA.

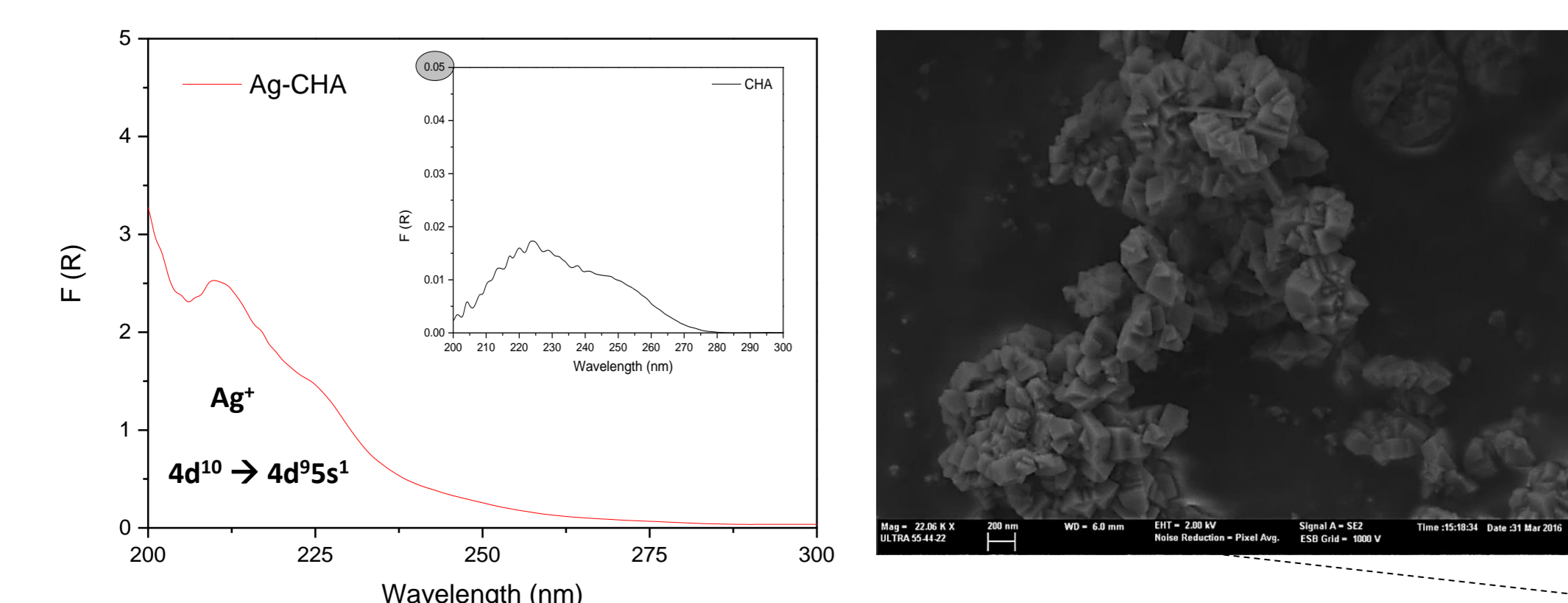


Fig. 2. UV-vis spectra of Ag-CHA and CHA (left) and FESEM of CHA (right).

Preliminary results – XAS

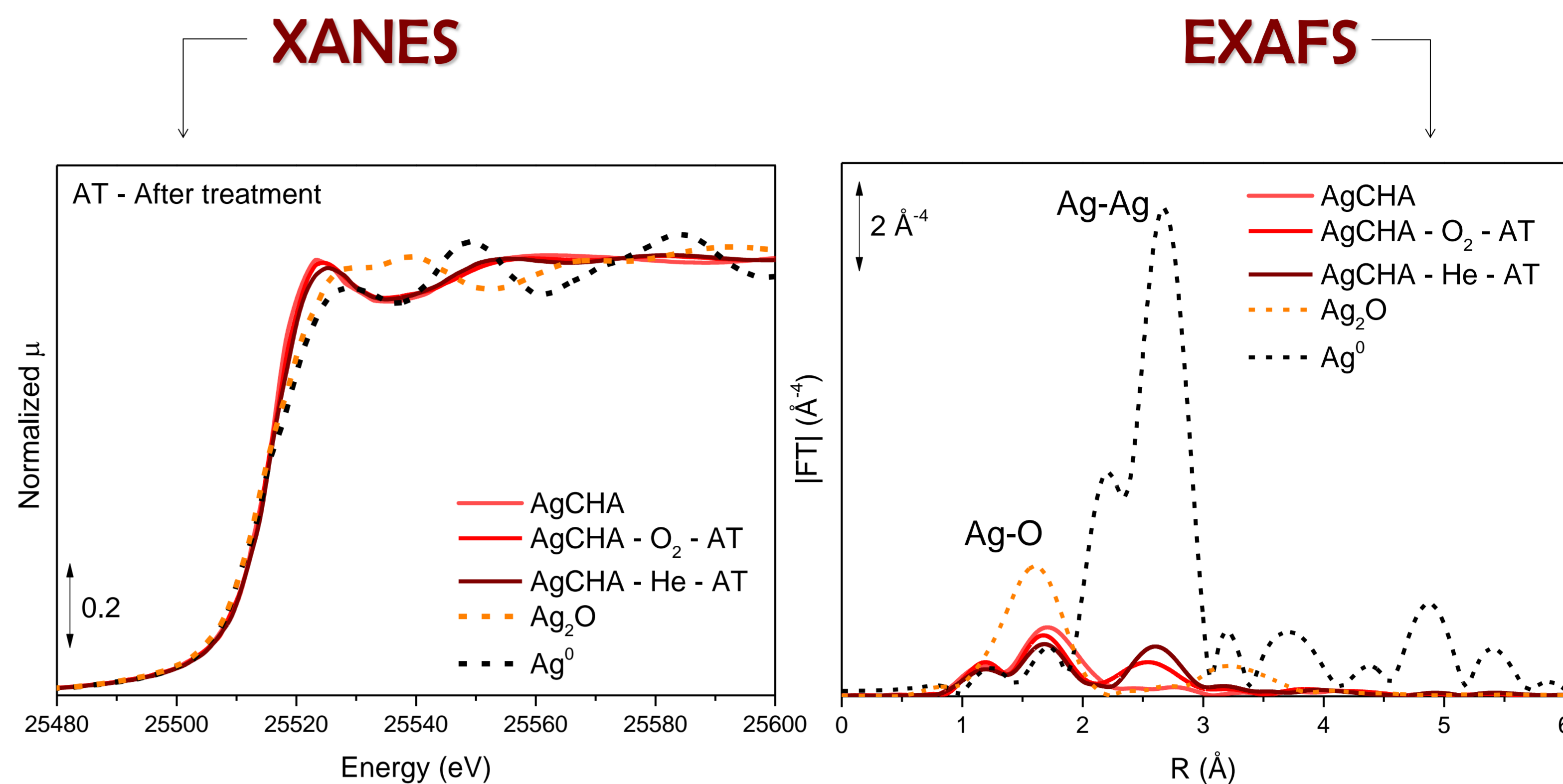


Fig. 3. XANES spectra (left) and |FTI| of the k^3 -weighted EXAFS spectra, no phase corrected, (right) of Ag-CHA sample at room temperature and after treatments under oxidative and inert atmosphere, compared to bulk Ag₂O and Ag.

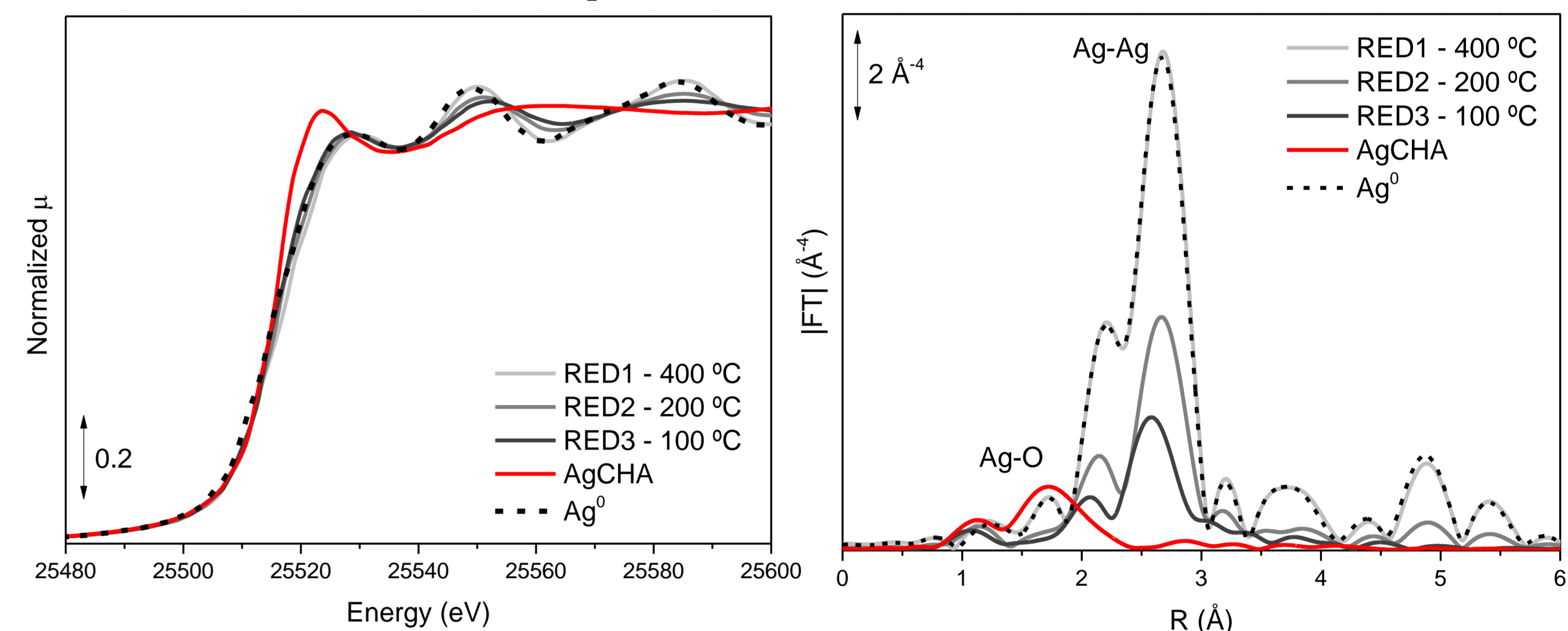
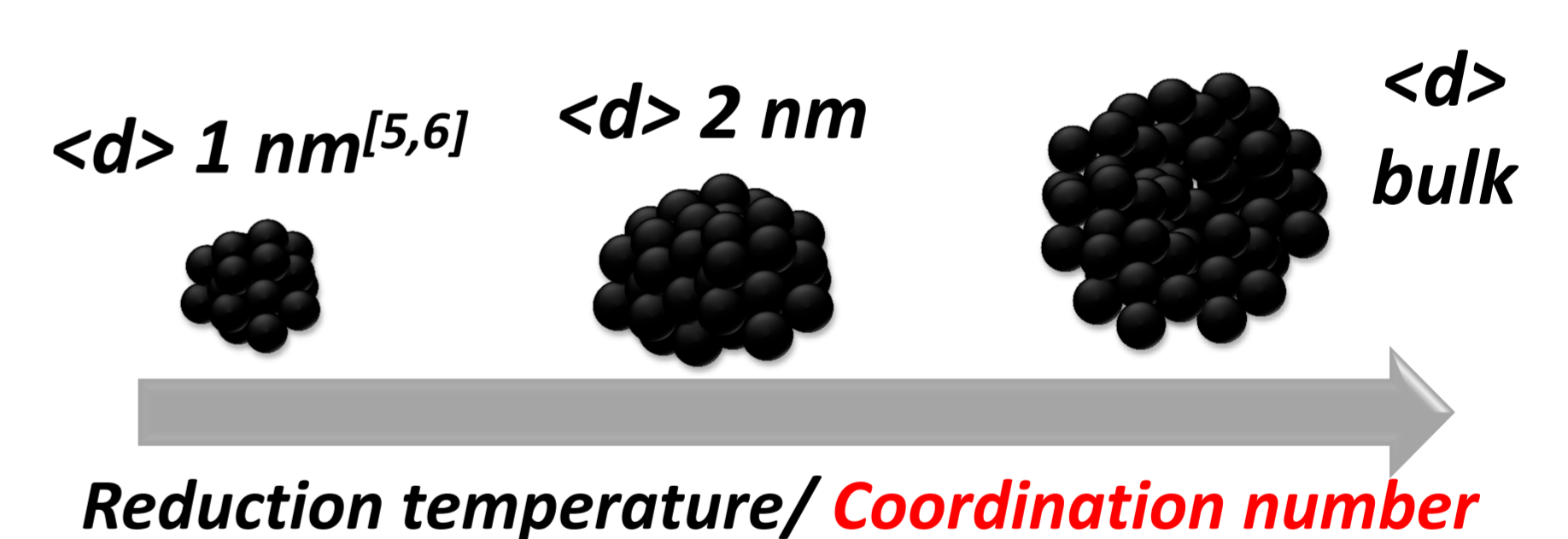


Fig. 4. XANES spectra (left) and |FTI| of the k^3 -weighted EXAFS spectra, no phase corrected, (right) of Ag-CHA sample after reduction in H₂ at different temperatures, compared to bulk Ag.

Table 1. Summary of the parameters optimized by fitting Ag-Ag distance of EXAFS data of sample after treatment in H₂ at different temperatures.

Sample	CN	R (Å)	σ^2 (Å ⁻²)	E ₀ (eV)	r-factor
AgCHA-400 H ₂	12.0 ± 0.6	2.860 ± 0.004	0.0094 ± 0.0005	2.5 ± 0.4	0.003
AgCHA-200 H ₂	8.9 ± 0.5	2.841 ± 0.005	0.0131 ± 0.0007	2.7 ± 0.5	0.004
AgCHA-100 H ₂	5.7 ± 0.7	2.780 ± 0.014	0.0147 ± 0.0018	0.3 ± 1.1	0.021

k-range: 2.3-11.8
R-range: 2-3 Å
Fitted in k^1, k^2, k^3
Ag powder
S₀²: 0.73



Conclusions

The nature of the silver species occluded within CHA zeolite has been established by a XAS study. It has been observed that after ion-exchange silver is present as Ag⁺ in the CHA zeolite. The thermal reduction of the sample under H₂ results in the reduction of Ag⁺ to Ag⁰ and in the formation of silver nanoparticles with different size depending on the temperature, being the nanoparticles formed at 400 °C larger than those formed at 100 °C. Moreover, thermal treatments under air and He do not change the silver oxidation state of Ag species. However, the appearance of a second coordination shell evidences the formation of a complex local structure around silver in these systems.

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