

Supporting Information

From isolated Ag⁺ ions to aggregated Ag⁰ nano-clusters in silver-exchanged ETS-10 molecular sieve: a reversible behavior

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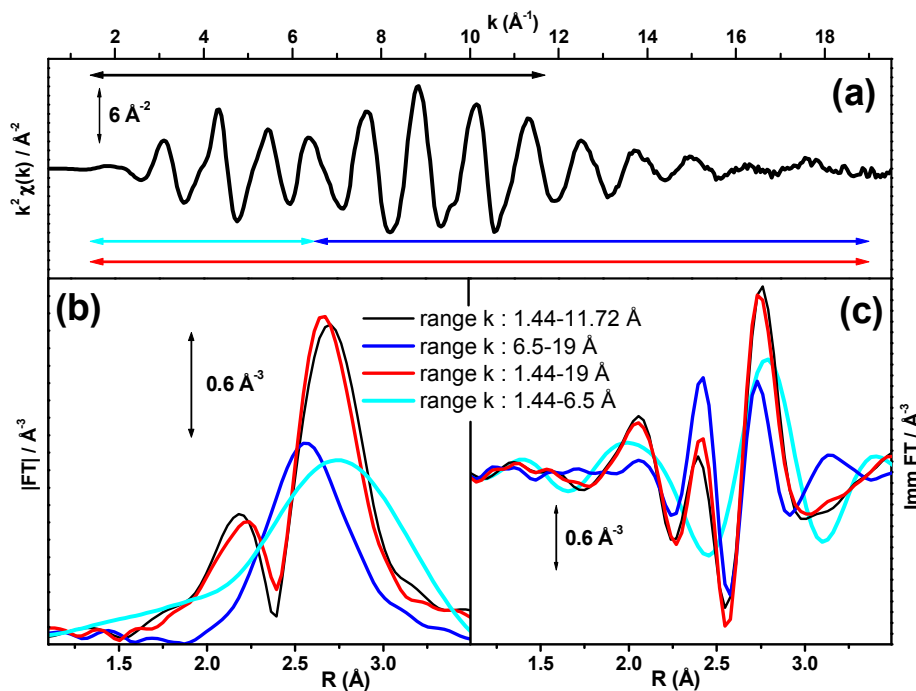


Figure S1. Part (a): experimental $k^2\chi(k)$ function of Ag foil model compound. Horizontal colored lines refer to the k -intervals used to perform the FT reported in parts (b) and (c). Part (b): corresponding modulus of the FT performed using different k intervals, as described in the legend. Part (c): as part (b) for the corresponding imaginary parts of the FT.

Figure S1a reports the experimental $k^2\chi(k)$ function of Ag foil model compound. From its behavior it is evident that the EXAFS oscillations behave differently in the 2-7 \AA^{-1} and in the 8-19 \AA^{-1} k -intervals. When the FT of the $k^2\chi(k)$ function is performed using a k -interval that includes a significant fraction of the two k -regions described above, the Ag-Ag first shell contribution in R -space (1.8-3.2 \AA) exhibits a double peak-shaped feature, see black and red curves in Figure S1b. This “strange” feature disappears by performing the FT in the 1.44-6.5 \AA^{-1} interval (cyan curve) or in the 6.5-19.0 \AA^{-1} interval (blue curve). Of course also the k -weight plays a relevant role in the first shell shape as it balances the contribution of the two intervals. Such k -interval dependent features of the modulus of the FT are typical of first shell scattering atoms with high Z numbers, which scattering amplitudes are modulated in k -range, as shown e.g. for the As-In scattering as reported elsewhere.¹⁻³ Of particular interest, in Ref.³ is the comparison between the FT (3.0–20.0 \AA^{-1} interval) of the EXAFS spectra, performed in transmission mode, on $\text{InAs}_x\text{P}_{1-x}$ bulk compounds (Figure 1b showing an As-In single peaked contribution) and the FT (3.0–10.0 \AA^{-1}) of the EXAFS spectra, performed in fluorescence mode, on $\text{InAs}_x\text{P}_{1-x}/\text{InP}$ quantum Wells (Figure 1d showing an As-In double peaked contribution).

Table S1 summarizes the first shell EXAFS data analysis on the Ag-ETS-10 samples reduced in H_2 atmosphere at 423 and 573 K. For all other samples, containing a significant fraction of both isolated Ag^+ cations and clustered Ag^0 species a quantitative EXAFS data analysis could not be safely performed, for the reasons outlined in the main text.

Table S1: Results of the first shell EXAFS analysis performed on Ag-ETS-10 samples reduced in H_2 atmosphere at increasing temperature.

Reduction T (K)	N	R (\AA)	S^2 (\AA^2)	E_0 (eV)
423	10.2 ± 0.6	2.85 ± 0.01	0.0117 ± 0.0006	2.6 ± 0.4
573	11.2 ± 0.6	2.85 ± 0.01	0.0110 ± 0.0005	2.7 ± 0.4

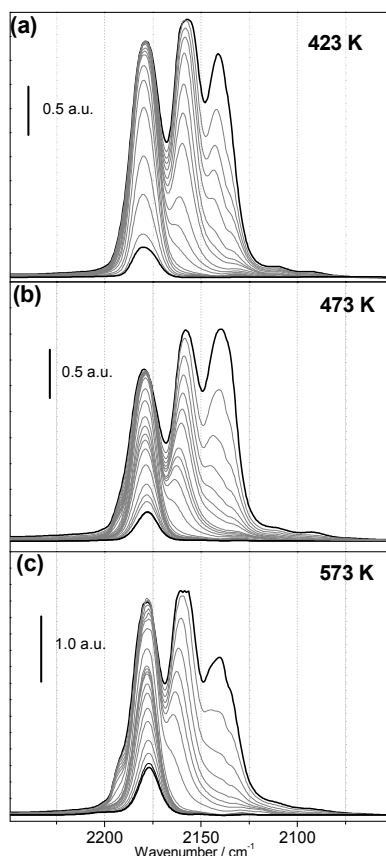


Figure S2. FTIR spectra of adsorbed CO at 100 K at increasing equilibrium pressure on Ag⁺ exchanged ETS-10 previously outgassed under dynamic vacuum at different temperature: part (a) 423 K, part (b) 473 K and part (c) 573 K.

Figure S2 reports the FTIR spectra obtained upon dosing CO at 100 K on the Ag-ETS-10 sample thermally activated at increasing temperatures, up to 573 K. The main features are basically comparable in all cases, testifying that IR spectroscopy of adsorbed CO is not able to discriminate between the three samples. UV-Vis remains the best technique to highlight the presence of a small amount of aggregated Ag, nanoparticles (see Figure 6 in the main text), while EXAFS (see Figure 4e-f in the main text) starts to be informative at slightly higher concentration of aggregated species.

References

- (1) Lamberti, C.; Bordiga, S.; Boscherini, F.; Pascarelli, S.; Schiavini, G. M. *Appl. Phys. Lett.* **1994**, *64*, 1430-1432.
- (2) Lamberti, C.; Bordiga, S.; Boscherini, F.; Mobilio, S.; Pascarelli, S.; Gastaldi, L.; Madella, M.; Papuzza, C.; Rigo, C.; Soldani, D.; Ferrari, C.; Lazzarini, L.; Salviati, G. *J. Appl. Phys.* **1998**, *83*, 1058-1077.
- (3) Pascarelli, S.; Boscherini, F.; Lamberti, C.; Mobilio, S. *Phys. Rev. B* **1997**, *56*, 1936-1947.