Supplementary Information

Activation of Atomically Precise Silver Clusters on Carbon Supports for Styrene Oxidation Reactions

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**Fig. S1.** XPS spectra for activated Ag_{25}/carbon catalyst at 350 °C; (a) S 2p, and (b) O 1s spectra.

**Fig. S2.** EXAFS data in (a) k-space and (b) R-space, for as-prepared Ag_{25}/carbon catalyst.
Fig. S3. EXAFS data in k-space (a-c) and R-space (d-f) for activated Ag$_{25}$/carbon catalysts at 250 °C (a,d), 350 °C (b,e), and 450 °C (c,f) respectively.
Table S1. Stability of dispersed Ag$_{25}$L$_{18}^{-}$ clusters as determined by the preservation of optical transitions in UV-Vis measurements.

| Solvent property | Longevity (in days) at different storage temperature |
|------------------|-----------------------------------------------------|
| **Solvent**      | **Dielectric constant ($\varepsilon$)** | **22-24 °C (ambient)** | **~4 °C (cold)** |
| THF              | 7.58                                  | 2                      | 24                   |
| DCM              | 8.93                                  | 4                      | 31                   |
| DMF              | 36.7                                  | 6                      | 120                  |
| DMSO             | 46.7                                  | 10                     | 2*                   |

*Freezes up after 2 days.

Table S2. Multi-shell EXAFS fitting parameters for as-prepared Ag$_{25}$/carbon catalysts.

| Bond type | CN   | R/Å   | $\sigma^2$/Å$^2$ | $E_o$ shift /eV | R-factor |
|-----------|------|-------|-----------------|-----------------|----------|
| Ag-S      | 1.08(5) | 2.401(6) | 0.00272(2) | -4.0(8) | 0.0066 |
| Ag-Ag     | 0.5(1) | 2.81(2) | 0.00900(3) | -4.0(8) |          |