Supplementary information

Mechanism of Cs Precursor Effect on Cs-Ag/Al_2O_3: Tuning Oxygen Activation for Ethylene Epoxidation

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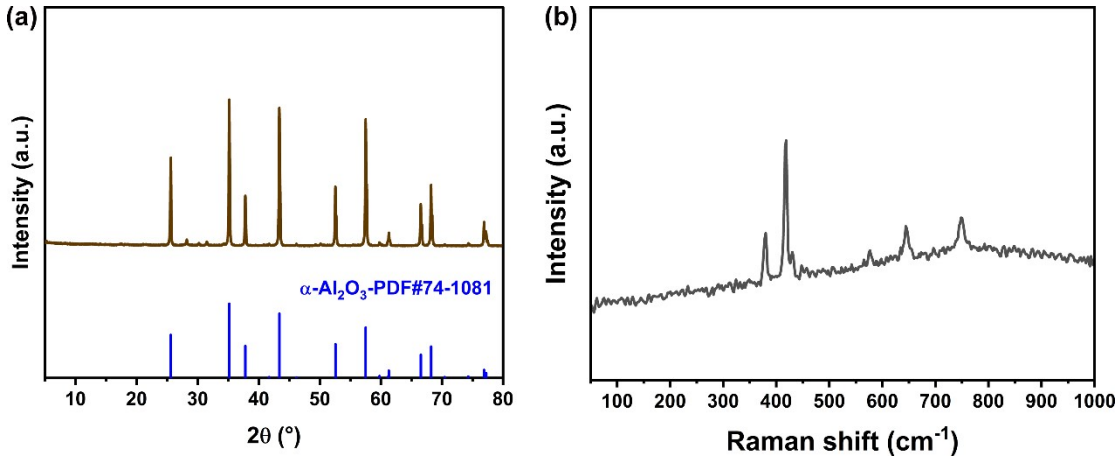

Fig. S1 (a) XRD pattern and (b) Raman spectra for pure Al_2O_3 sample.

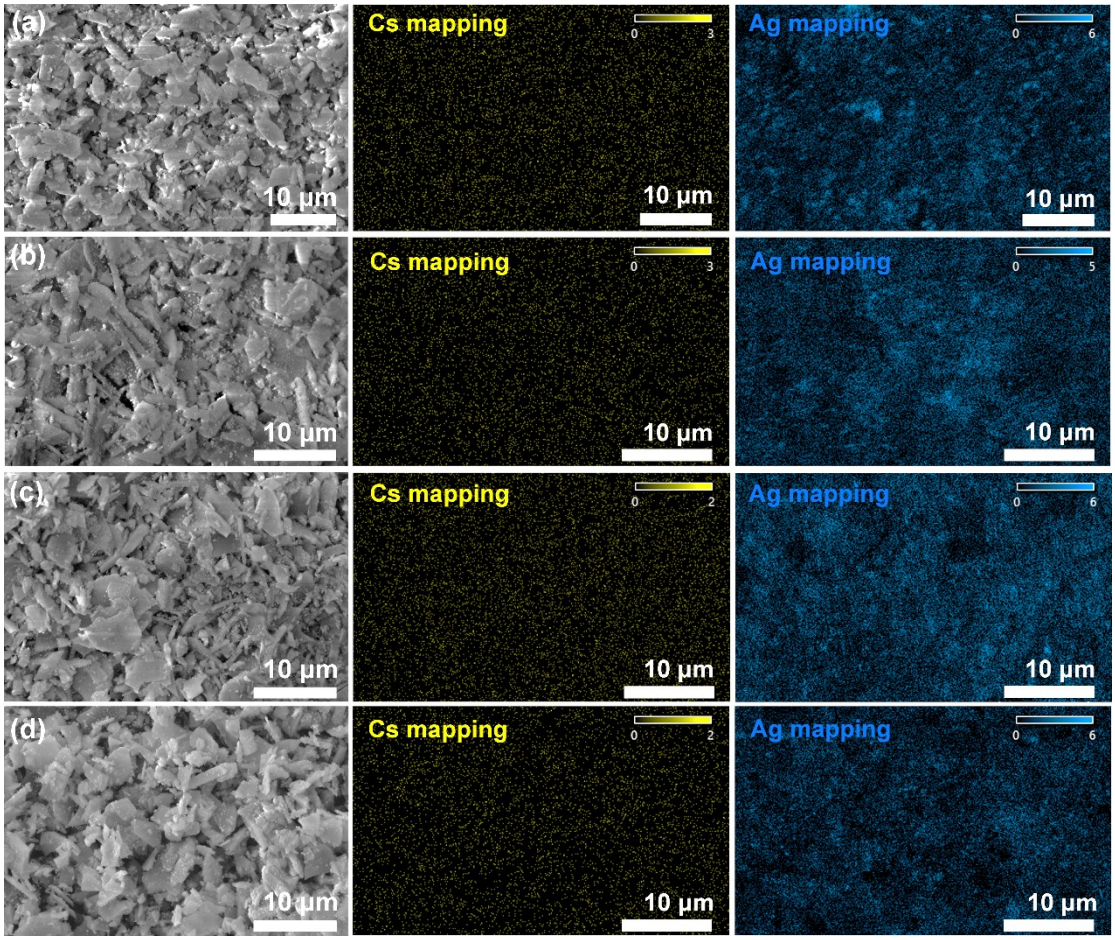

Fig. S2. SEM images with EDX maps of as-prepared Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (samples A, B and C).

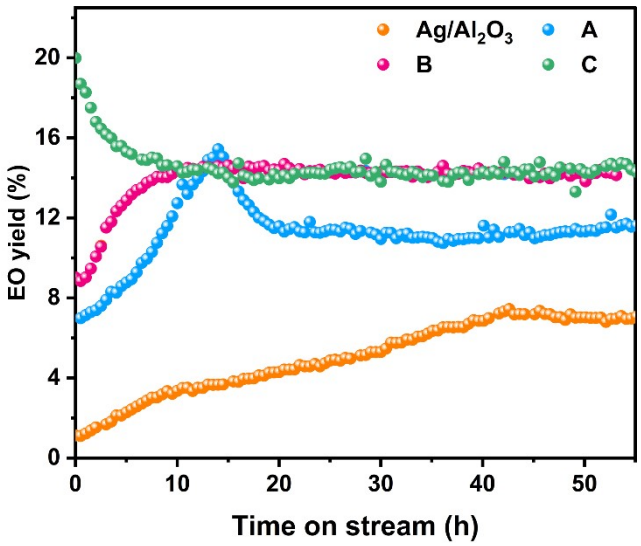

Fig. S3. EO yield during ethylene epoxidation along with the time on stream over Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (A, B and C) catalysts. Reaction conditions: T = 225 °C, P = 20 bar, C_2H_4:O_2:N_2 = 7.5 vol%/3.0 vol%/89.5 vol% and GHSV = 5100 h^{-1}.

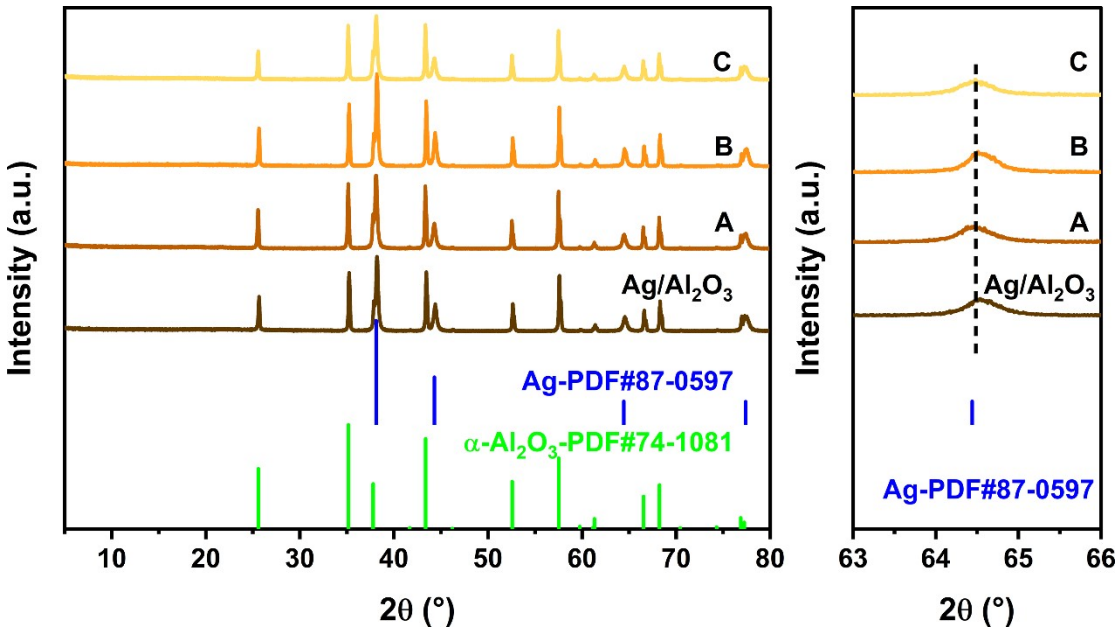

Fig. S4. XRD patterns of the used Al_2O_3, Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (A, B and C) samples.

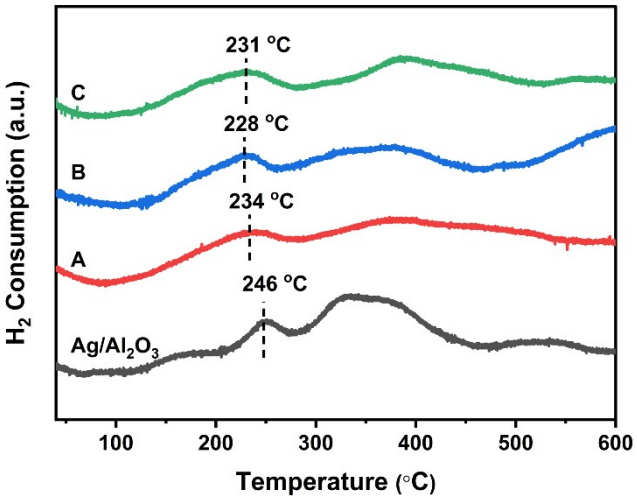

Fig. S5. H_2-TPR profiles of the used Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (A, B and C) samples.

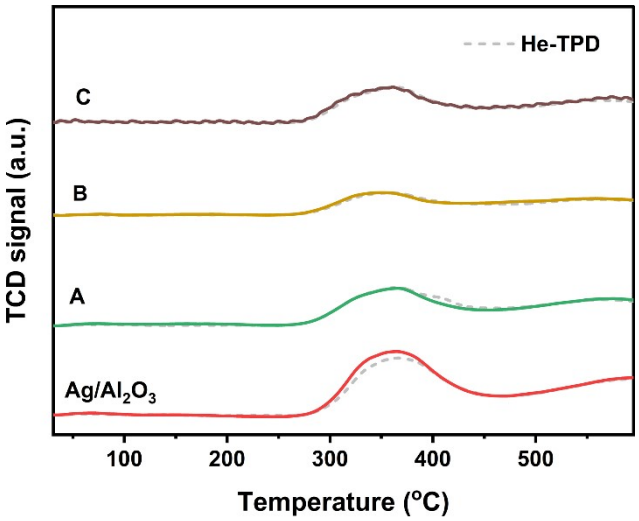

Fig. S6. C_2H_4-TPD and He-TPD (gray dot line) profiles of Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (samples A, B and C).

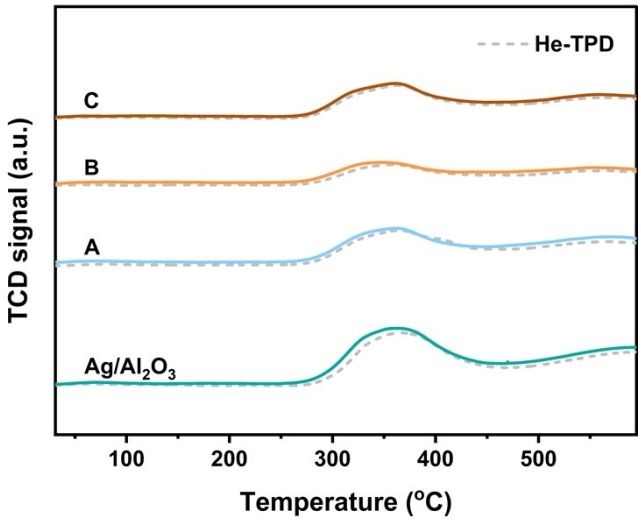

Fig. S7. CO_2-TPD and He-TPD (gray dot line) profiles of Ag/Al_2O_3 and Cs-promoted Ag/Al_2O_3 (samples A, B and C).

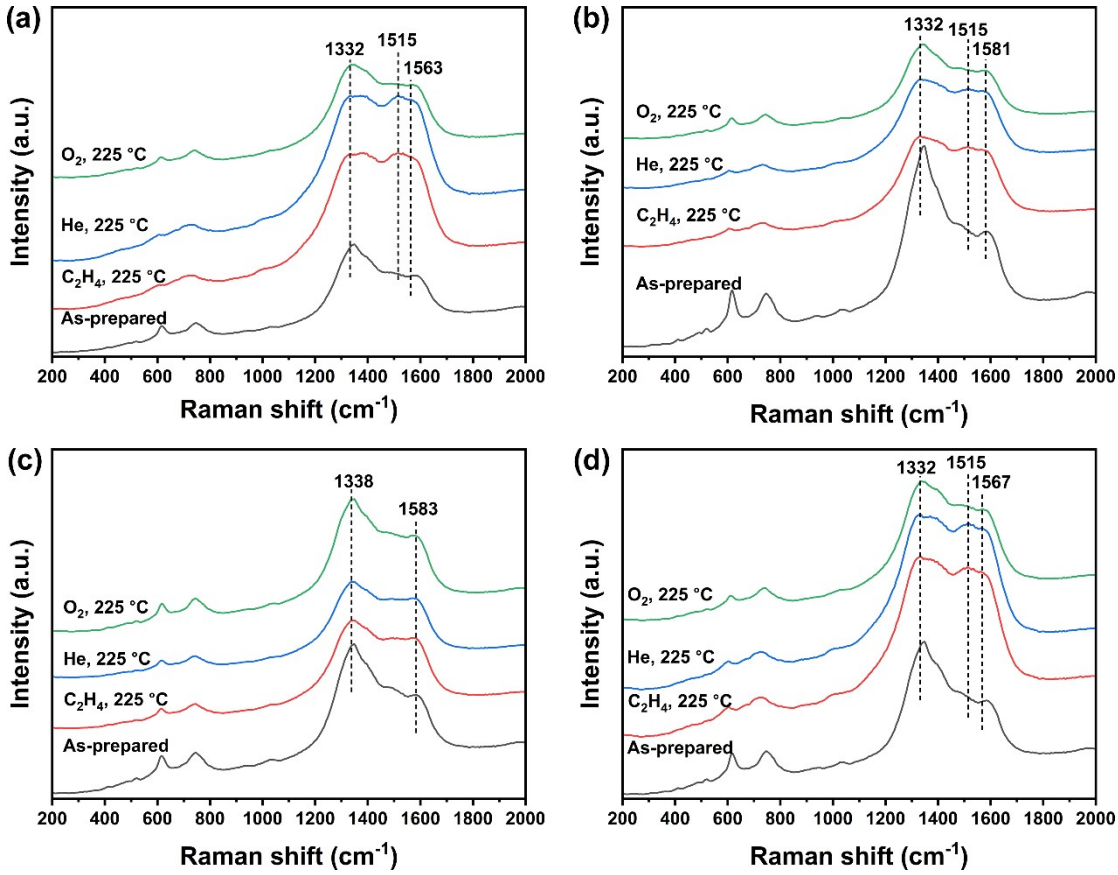

Fig. S8. Raman spectra during ethylene adsorption over (a) Ag/Al_2O_3, (b) sample A, (c) sample B, and (d) sample C.

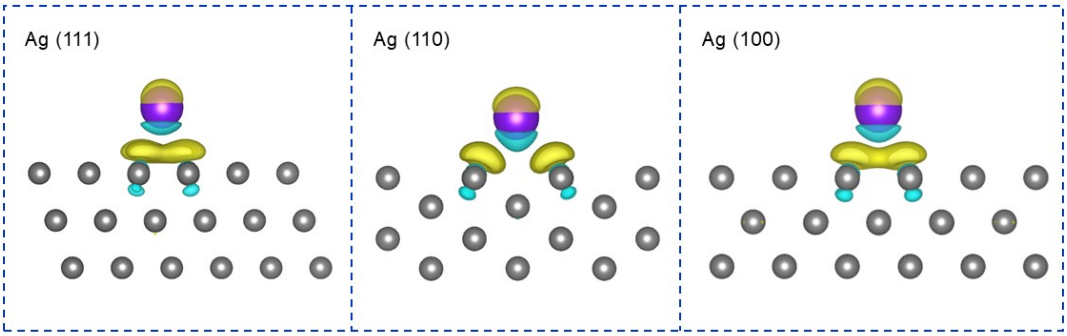

Fig. S9. Isosurfaces (isovalue = 0.001) of the charge density difference of the Cs-modified Ag (111), Ag (110) and Ag (100) surfaces using density functional theory (DFT) calculations. Gray and purple spheres represent Ag atoms and Cs atoms, respectively. Yellow and blue isosurfaces correspond to charge accumulation and charge depletion regions, respectively.

Table S1. Physical properties of the as-prepared Ag/Al_2O_3 and A, B, C catalysts.

Sample	Ag (wt%)[a]	Cs (wt%)[a]	As-prepared		Used	
			Ag d_{XRD} (nm)[b]	Ag d_{SEM} (nm)[c]	Ag d_{XRD} (nm)[b]	Ag d_{SEM} (nm)[c]
Ag/Al_2O_3	13.12	-	38.9	159 ± 1	44.8	165 ± 4
A	12.97	0.04	35.6	88 ± 1	41.2	128 ± 2
B	13.24	0.04	33.4	80 ± 1	45.1	132 ± 3
C	12.93	0.04	33.2	93 ± 1	40.7	125 ± 3

[a] Determined by ICP-OES.
[b] The Ag particle size was estimated based on the XRD line broadening of the Ag (220) diffraction peak.
[c] The Ag particle size was estimated from SEM images by counting 250-300 silver particles across at least three different regions, assuming a spherical morphology.

Table S2. O_2-TPD data for Ag/Al_2O_3 and A, B, C samples.

Sample	I_1/I_2 ratio	O_2 desorption (μmol g_{cat}^{-1})[a]
Ag/Al_2O_3	0.99	13.5
A	0.87	21.7
B	0.93	24.6
C	0.92	21.5

[a] Determined by the integrated area of the reduction peak from 150 to 350 °C.

Computational Details

All DFT calculations were carried out using the CP2K Code.[1] Perdew-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA) was applied to treat exchange correlation functions. The Geodecker–Teter–Hutter (GTH) pseudopotentials were implemented to describe core electrons, with the hybrid Gaussian and plane waves framework (GPW).[2] The valence molecular orbitals were expanded using molecularly optimized (MOLOPT) Gaussian-type basis sets.[3] A Monkhorst–Pack 3 × 3 × 1 K-point sampling was used, with a 500 Ry cutoff energy. Three kinds of Cs-doped metallic silver facets ((111), (110), (100)) are considered.[4] These structures were optimized within periodic boundary conditions using three layers of a 4 × 4 unit cell. Isosurfaces of the charge density difference of the Cs-modified Ag (111), Ag (110) and Ag (100) surfaces were shown in Fig. S9.

References

1. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach, *Computer Physics Communications*, 2005, **167**, 103-128.
2. S. Goedecker, M. Teter, J. Hutter, Separable dual-space Gaussian pseudopotentials, *Physical Review B*, 1996, **54**, 1703-1710.
3. J. VandeVondele , J. Hutter, Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases, *The Journal of Chemical Physics*, 2007, **127**, 114105.
4. T. Pu, A. Setiawan, A. C. Foucher, M. Guo, J. M. Jehng, M. Zhu, M. E. Ford, E. A. Stach, S. Rangarajan, I. E. Wachs, Revealing the Nature of Active Oxygen Species and Reaction Mechanism of Ethylene Epoxidation by Supported Ag/α-Al2O3 Catalysts, *ACS Catalysis*, 2024, **14**, 406-417.