Supporting Information

Metal-oxide interaction modulating activity of active oxygen species

in atomically dispersed silver catalyst

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Experimental Section

1.1. Catalyst preparation.

The supported Ag catalysts were synthesized by impregnation method. Silica (SiO_2, Qingdao Haiyang Chemicals Co.) and pseudo boehmite ($AlOOH \cdot nH_2O$ with a Brunauer-Emmett-Teller (BET) area of 300 m^2/g, Macklin) were calcinated in a muffle furnace at high temperature (800 °C) for 5 h to obtain the SiO_2 support[1] and γ-Al_2O_3 support,[2] to reduce the effect of support acidity as much as possible.[3] The oxide powders were mixed with Ag nitrate ($AgNO_3$) solution with Ag weight loading at 0.5 wt%. Then the solution was dried in air at 60 °C under magnetic stirring and subsequently dried at 110 °C overnight. The dried powders were pretreated in O_2 at 500 °C with a ramping rate of 2 °C/min and a dwell time of 2 h before each catalytic test and characterization.

1.2. Catalyst Characterization.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded on a JEOL JEM-ARM300F microscope operating at 200 kV. To avoid the influence of ethanol dispersion solution on the structure of supported Ag species, the catalyst powders were directly dispersed on carbon films supported on copper grids. In situ Raman spectroscopy tests were performed on a micro-laser confocal Raman spectrometer of model LabRAM HR800 (HORIBA JOBIN YVON corporation) with a laser excitation of 532 nm. 500 °C and 250 °C were selected as the test temperature for reaction with CO and ethylene respectively, according to corresponding catalytic activity. The spectrometer was equipped with a high-temperature reaction cell. X-ray diffraction (XRD) experiments were carried out on the Empyrean diffractometer using Cu Kα (λ = 1.5406 Å) radiation source and scanning rate of 10°/min. X-ray photoelectron spectroscopy (XPS) analyses were performed on a SPECS spectrometer with an Al Kα source (1486.6 eV) operated at 300 W. X-ray absorption near-edge structure (XANES) measurements at the Ag K-edge (25517 eV) were performed in the transmission mode with the Si (311) monochromator at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. CO

temperature-programmed reduction (CO-TPR) and C_2H_4 temperature-programmed surface reaction (C_2H_4-TPSR) were performed in a Micromeritics AutoChem II 2920. 0.1 g sample was put into the U tube, which was heated from 25 to 500 ℃ at a rate of 5 ℃/min under a flow of a 5% CO/Ar mixture (10% C_2H_4/Ar mixture). Before a TP(S)R run, the samples were pretreated in O_2 at 500 ℃ for 1 h and then cooled to room temperature (RT). Quasi in situ electron paramagnetic resonance (EPR) experiments were carried out on a Bruker A200 spectrometer. The powders were loaded into the quartz EPR tube and treated in O_2 at 500 ℃ for 1 h and 5% O_2/Ar after cooling to RT. The experimental temperatures applied were -150 ℃.

1.3. Catalytic test.

CO oxidation reaction performance was evaluated using a homemade fixed-bed microreactor, in which catalysts were loaded into a quartz tube with an inner diameter of 4 mm. The reactant was composed of 1% CO and 20% O_2 (volume ratio), balanced with N_2. The outlet gas was analyzed online using an Agilent GC490 chromatograph. Before activity tests, each catalyst was pretreated in reaction gas at RT for 1 h. Ethylene oxidation performance was evaluated using the same microreactor. The gas feed was composed of 22% C_2H_4/11% O_2/22% He/45% N_2 and the outlet gas was analyzed online using an Agilent GC490 chromatograph. Before activity tests, each catalyst was pretreated in the reaction gas at RT for 1 h. Total weight hourly space velocity (WHSV) was 12000 mL per gram catalyst per hour (12000 mL·h^{-1}·g^{-1}) and 2000 - 4000 mL·h^{-1}·g^{-1} for CO oxidation and ethylene oxidation, respectively. To compare the difference of the intrinsic activity, weight hourly space velocity (WHSV) of 4000 mL·h^{-1}·g^{-1} and 2000 mL·h^{-1}·g^{-1} were used for the Ag_1/SiO_2 and Ag_1/Al_2O_3 catalysts, respectively, ensuring the similar ethylene conversion within 1% - 5% at the same temperature range (100 - 300 ℃).
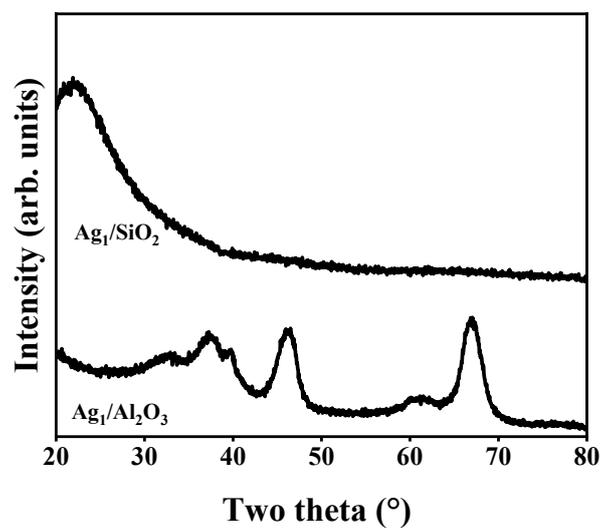
Figures
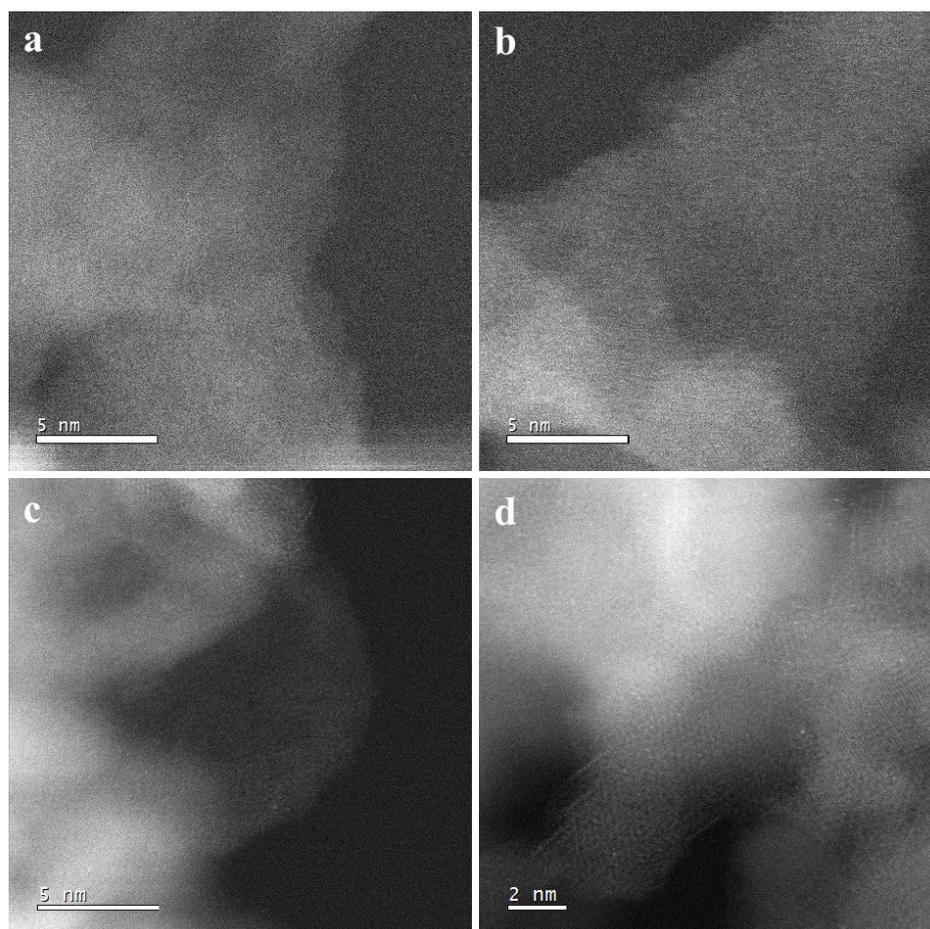

Fig. S1. XRD patterns of Ag_1/SiO_2 and Ag_1/Al_2O_3 catalysts.

Fig. S2. HAADF-STEM images of Ag_1/SiO_2 catalyst (a, b) and Ag_1/Al_2O_3 catalyst (c, d).
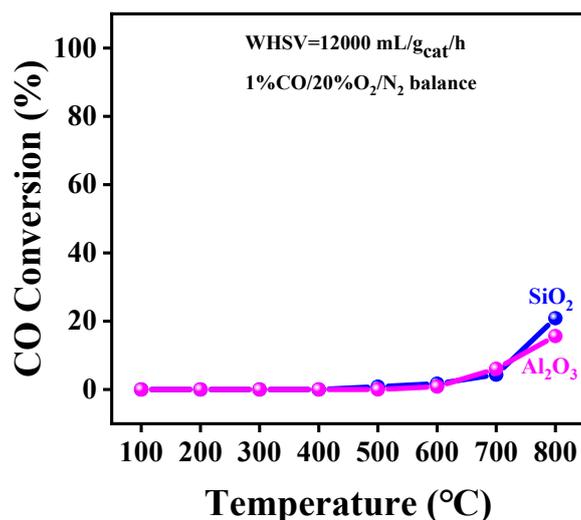
Fig. S3. CO conversion of Ag_1/Al_2O_3 and Ag_1/SiO_2 catalysts; Reaction conditions: 1% CO/20% O_2/79% N_2, WHSV = 12000 mL·h^{-1}·g^{-1}.
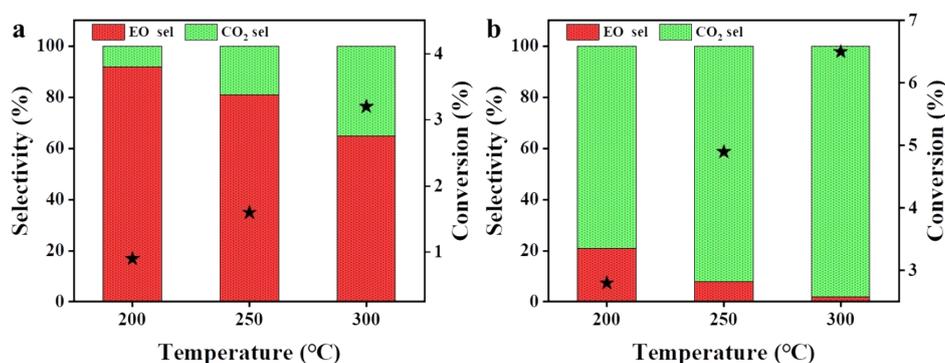
Fig. S4. Ethylene conversion and ethylene oxide selectivity of (a) Ag_1/Al_2O_3 and (b) Ag_1/SiO_2 catalysts in ethylene epoxidation reaction; Reaction conditions: 22% C_2H_4/11% O_2/22% He/45% N_2, WHSV = 3000 mL·h^{-1}·g^{-1}.
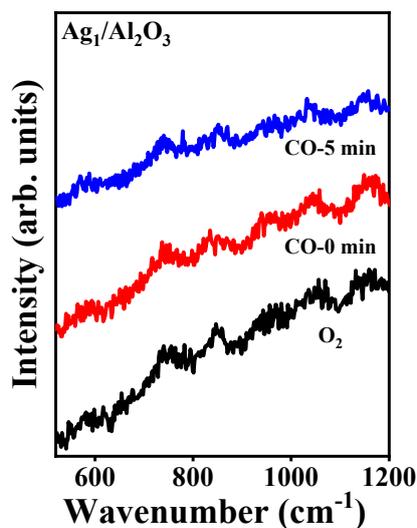
Fig. S5. In situ Raman spectra of Ag_1/Al_2O_3 catalysts in 5% CO at 500 °C.
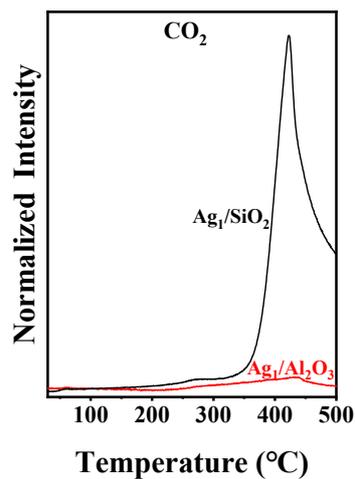
Fig. S6. C_2H_4-TPSR signals of Mass = 44 for CO_2.
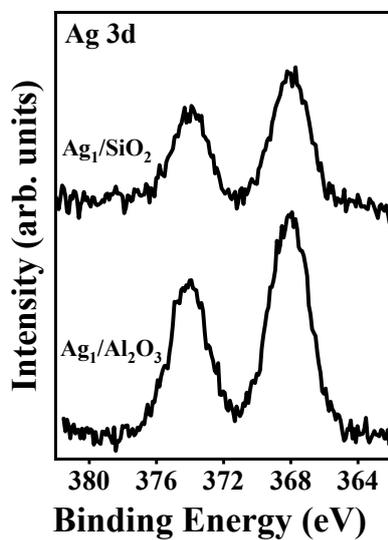
Fig. S7. Ag 3d XPS spectra of Ag_1/SiO_2 and Ag_1/Al_2O_3 catalysts.
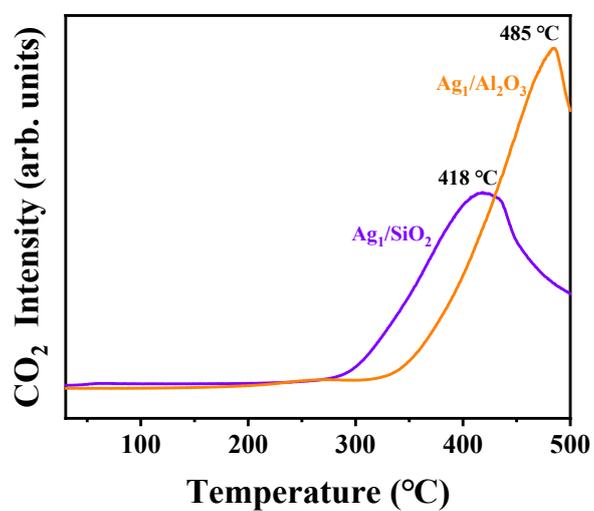

Fig. S8. CO-TPR results of Ag_1/SiO_2 and Ag_1/Al_2O_3 catalysts.

Reference

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