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SUPPORTING INFORMATION

Gas Phase Selective Propylene Epoxidation over La_2O_3-Supported Cubic Silver Nanoparticles

Bin Yu[†], Tuğçe Ayvalı[†], Zhi-Qiang Wang, Xue-Qing Gong, Abdulaziz A. Bagabas and S. C. Edman Tsang*

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[†] Equal contribution
* Corresponding author: edman.tsang@chem.ox.ac.uk

Experimental Methods

Synthesis of Ag/Ln_2O_3 Catalysts

The conventional Ag catalysts with different supports were prepared in a one-pot polyol method.[1] A chosen series of commercially available Sigma-Aldrich lanthanide oxides (Ln_2O_3) of few m^2g^{-1} surface areas were used as metal oxide supports for the Ag based catalysts, which include La_2O_3 from early lanthanide group, Gd_2O_3, Eu_2O_3 from middle lanthanide group and Yb_2O_3, Lu_2O_3 from late lanthanide group. A commercial high surface area γ-Al_2O_3 ($150m^2g^{-1}$)[2] was used as the standard metal support for comparison. In a standard synthesis, 20 mL ethylene glycol (EG) was added into a 100 mL round bottom flask and heated to 130 °C under magnetic stirring. The EG was used as a reducing agent for the syntheses of Ag and was pre-heated to 130 °C to ensure the reduction rate is consistent for all synthesises. To prepare 5 wt% Ag catalysts, a known amount of PVP solution (1 M in EG), $AgNO_3$ solution (1 M in EG) and Ln_2O_3 solution (40 M in EG) were quickly added to the reactor respectively when the temperature reached to 130 °C (PVP to Ag molar ratio is 10 to 1). The mixture was reacted for 1hr at 130 °C to allow all $AgNO_3$ be reduced to Ag^0, then cooled down to room temperature in ice-water bath to prevent further sintering. All the samples were collected by centrifugation (5000 rpm, 15 mins), then washed with acetone (once) and water (five times) to remove the excess amount of EG and PVP and dried in vacuum.

Synthesis of Morphology Controlled Ag Nanoparticles Supported on La_2O_3

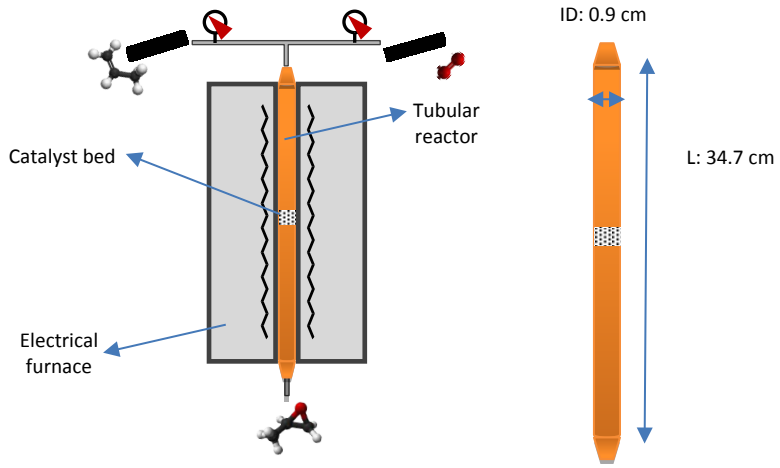
Morphology controlled Ag nanoparticles were synthesised using a modified polyol process reported by Xia and co-workers.[3,4] For Ag nanocube preparation, in a standard synthesis, 5 mL ethylene glycol (EG) was added into a 50 mL round bottom flask and heated under magnetic stirring for 30 mins in an oil bath pre-set to 150 °C. 0.06 mL NaSH (3mM in EG) was quickly injected into the solution when the temperature reached to 150 °C. Two minutes later, 0.5 mL HCl solution (3mM in EG) was quickly injected into the heated solution followed by the addition of 1.25 mL PVP solution (20mg/mL in EG, MW ≈ 55,000). Both NaSH and HCl were used as capping agent to enable a more favourite growth of Ag(100).[5] After another 2 min, 0.4 mL silver trifluoroacetate solution (282 mM EG, ≥ 99.99%) was quickly added into the heated mixture. During the entire process, the flask was capped with a glass stopper except during the addition of reagents. The Ag nanocubes were achieved after 35 min reaction time. The reaction solution was quenched by placing the reaction flask in an ice-water bath to prevent further reaction. All the samples were collected by centrifugation (2200 rpm, 20 mins). The Ag nanocubes were then washed with acetone for 5 times to remove the remaining precursor, EG, excess capping agent and PVP. The Ag nanospheres were prepared using a similar method to Ag nanocubes synthesis but without the addition of capping agents (NaHS and HCl). All the morphology-controlled Ag nanoparticles were kept in acetone for further use. It was found that Ag particles have maintained a stable morphology in acetone for at least 3 months. The morphology controlled Ag/Ln_2O_3 catalysts were then prepared using a volumetric impregnation method. The catalytic supports are pre-treated as follows: The La_2O_3 (≥ 99% purity, Sigma Aldrich) was calcined at 600 °C for 4 hrs in N_2 in a tubular furnace. The Al_2O_3 (activated, neutral, Brockmann Activity, Sigma-Aldrich) was calcined at 500°C for 4 hrs in air in a

tubular furnace. In a typical preparation, a known amount of concentrated Ag nanoparticles solution was mixed and stirred with a certain amount of pre-treated supports. The obtained products were aged at room temperature under N_2 environment in dark for 4 hrs then dried at 100 °C. All the prepared catalysts were stored under N_2 environment in dark to prevent further oxidation or interaction with environmental water vapour.

It is noted that these Ln_2O_3 supports as well as Al_2O_3 have non-porous 2D structures; therefore mass transfer (internal diffusion) limitation is not anticipated to play a significant role. In addition, the use of reducible active metal oxides as support was not carried out since they not only transfer oxygen to interface but also very active to oxidise the surface species to combustion products by coupling with the facile change in oxidation state of metal ions. On the other hand, most lanthanide oxides with metal f-orbitals contraction show ionic character with exception of Ce and Pr which display redox properties as that of transition metals (due to their unique electronic configurations so they were not tested for this work).

Catalytic testing

In a standard reaction, 100 mg of powder catalyst was packed/sandwiched between two quartz wool (catalyst bed density: 0.393 g/cm^3) in the middle stage of a tubular reactor having 34.7 cm length and 0.9 cm internal diameter (ID) (Scheme 1).



Scheme 1. Illustration of tubular reactor

The catalysts were pre-reduced at 250 °C for 2 hrs in 10% hydrogen in helium at a constant flow rate of 30 mL/min in the reactor before starting the reaction. For the propylene epoxidation reaction, the composition of the feeding gas mixture was 5% C_3H_6 in helium and 5% O_2 in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/mins, which was delivered from the top of the reactor. A temperature program was used, beginning at 100 °C, at each reaction temperature, the reaction time test was kept for 1 h allowing the GC to analysis the reaction products.

$$\%Propylene\ Conversion = \frac{\frac{1}{3}x[CO_2] + [C_3H_6O]}{[C_3H_6]_{in}} X100$$

or

$$\%Propylene\ Conversion = \frac{[C_3H_6]_{in} - [C_3H_6]_{out}}{[C_3H_6]_{in}} X100$$

$$\%PO\ Selectivity = \frac{[C_3H_6O]}{\frac{1}{3}x[CO_2] + [C_3H_6O]} X100$$

$$\%PO\ Formation\ Rate = \frac{mol\ of\ PO\ produced}{gram\ of\ catalyst\ x\ second} X100$$

Characterisation

Powder X-Ray Diffraction (XRD)

The powder X-ray diffraction was performed on a PANalytical X PRO Diffractometer with Cu K_α radiation (wavelength $\lambda = 1.5406$ Å) produced by a generator operating at 40 kV and 40 mA. Profiles were measured from $\theta = 20 - 90°$. Colloidal samples (morphology controlled Ag nanoparticles) were prepared by depositing a concentrated ethanolic dispersion of PVP supported nanoparticles on the surface of a glass slide. The solvent was evaporated in vacuum, leaving a thin film of sample with an even thickness and smooth surface. Supported sample were prepared by covering a glass XRD plate with a thin, even layer of finely powdered sample. The powder was gently pressed with a glass slide to ensure a smooth surface.

Low and High Resolution Transmission Electron Microscopy (HR-TEM)

TEM was performed using the JEOL 2010 and JEOL 300 operating at 200 kV. Samples for TEM analysis were prepared by dispersing a small amount of material (typically 1 mg) in approximately 1 mL of ethanol. One drop of the dispersion was placed onto a copper grid (holey carbon supported on copper, 400 mesh) and the solvent evaporated in air prior to analysis. Average particles size distributions and the histogram were calculated from the measurement of at least 150 individual particles.

High-resolution HAADF STEM

High-resolution electron microscopy was carried out using an aberration-corrected JEOL ARM200F. The microscope was operated at 200 kV in HAADF-STEM mode with HAADF detector collection semi-angles from 73 to 236 mrad. The convergence semi-angle was 31.48 mrad with probe array sizes of 1024 by 1024 and a dwell time of 0.8 µs per pixel. The probe current was 11 pA.

X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed on a VG Escalab XPS Spectrometer operating under ultra-high vacuum (1×10^{-9} torr) using aluminium Kα radiation with an energy of 1486.3 eV. Samples were prepared by depositing a thin layer of finely ground powder onto a double-sided sticky carbon tab attached to each sample holder. Wide scan spectra were acquired from 1 to 1200 eV to identify elements present in the sample, and were compiled from 4 scans with 0.1 sec dwell time, a 1 eV step interval, and a pass energy of 50 eV. Spectra of specific regions were obtained for elements of interest and were compiled from 15 scans with a 0.4 sec dwell time, a 0.1 eV step interval, and a pass energy of 20 eV. Data was processed using CasaXPS peak fitting software and binding energies were referenced to the C 1s peak corrected to a value of 284.50 eV to eliminate charging effects in accordance with the method by Jansen and van Bekkum.[6]

Computational details

Density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP).[7] The exchange-correlation energy and potential were described by the generalized gradient approximation (GGA-PW91).[8,9] The kinetic energy cut-off for the wave function expanded in the plane-wave basis was set as 400 eV. To optimize the structures, the calculation was performed until the maximum force upon each relaxed atom was less than 0.05 eV/Å. The vacuum height was set as 15 Å to eliminate the interaction between neighbouring slabs. For bulk silver, the calculated lattice constant is 4.15 Å in better agreement with the experimental lattice constant (4.09 Å). The high-temperature A-form of La_2O_3 crystallizes in the experimental lattice constants are a = b = 3.939 Å and c = 6.136 Å.[10] The optimized bulk lattice constants for La_2O_3 are a = b = 3.920 Å and c = 6.093 Å, in good agreement with the experimental values.

The adsorption energy (E_{ads}) was calculated as follows:

$$E_{ads} = -(E_{total} - E_{substrate} - E_{gas\text{-}phase\ adsorbate})$$

where E_{total} is the calculated total energy of the adsorption system, $E_{substrate}$ is the energy of the clean substrate and $E_{gas\text{-}phase\ adsorbate}$ is the energy of the gas-phase molecule.

The oxygen vacancies energy (Evac) was calculated as follows:

$$E_{vac}(f) = E_{vac} + E_{\frac{1}{2}O_2} - E_{st}$$

where E_{vac} is the energy of the surface with one vacancy per supercell, $E_{\frac{1}{2}O_2}$ is half the energy of an O_2 molecule in the gas phase and E_{st} is the energy of the same supercell with no vacancy.

In order to study the adsorption of oxygen on silver surfaces, we used the following models: a 4×4 surface cell was used to construct a six-layer Ag(100) and Ag(111)slab. The top three layers of the Ag(100) and Ag(111) slab were allowed to relax. In addition, in order to study the oxygen vacancies energy on polar and nonpolar La_2O_3

surfaces, we used the following models: a 4×4 surface cell was used to construct a three-layer La_2O_3(001) slab. The top two layers of the La_2O_3(001) slab were allowed to relax.

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As the catalytic test conditions vary in the literature, it is preferred to report the activity of catalysts based on PO production rate which is defined as amount of produced PO (mol) per amount of catalyst (g or kg) per time (s or h). In order to be consistent with some previous works reported in the literature, catalytic activity of the prepared Ag/Ln_2O_3 samples is also presented as PO production rate (mol PO.g_{cat}^{-1}.s^{-1}) in the main text which can easily be converted to conversion. Herein, we provide an example calculation and a catalytic performance graph in terms of conversion and selectivity exhibited by Ln_2O_3 (Ln= La, Gd, Eu, Yb, Lu) and Al_2O_3-supported Ag nanospheres at 250 °C:

100 mg Ag nanospheres/La_2O_3 catalysts converts 1.4% propylene to propylene oxide with a selectivity of 15% at 250 °C and 1 atm under 20 ml/min flow of a gas mixture (5%C_3H_6 and 5%O_2 oxygen in 2:1 molar ratio). Density of propylene at 298K = 4.1163E-5 mol/ml

Volume of propylene inside the gas mixture (ml/s) = (20/3*2)*(5/100)/60 = 0.011111
Mol of propylene per second (mol/s) = 0.011111*(4.1163E-5) =4.5736E-7
Mol of PO formation per second (mol/s) = 4.5736E-7*(1.4/100)*(15/100) = 9.6046E-10
PO Rate (mol PO/g_{cat}.s) = 9.54875E-10/0.1 = 9.6046E-9
PO Rate (nmol PO/g_{cat}.s) = 9.6046E-9 = 9.6 nmol PO/g_{cat}.s

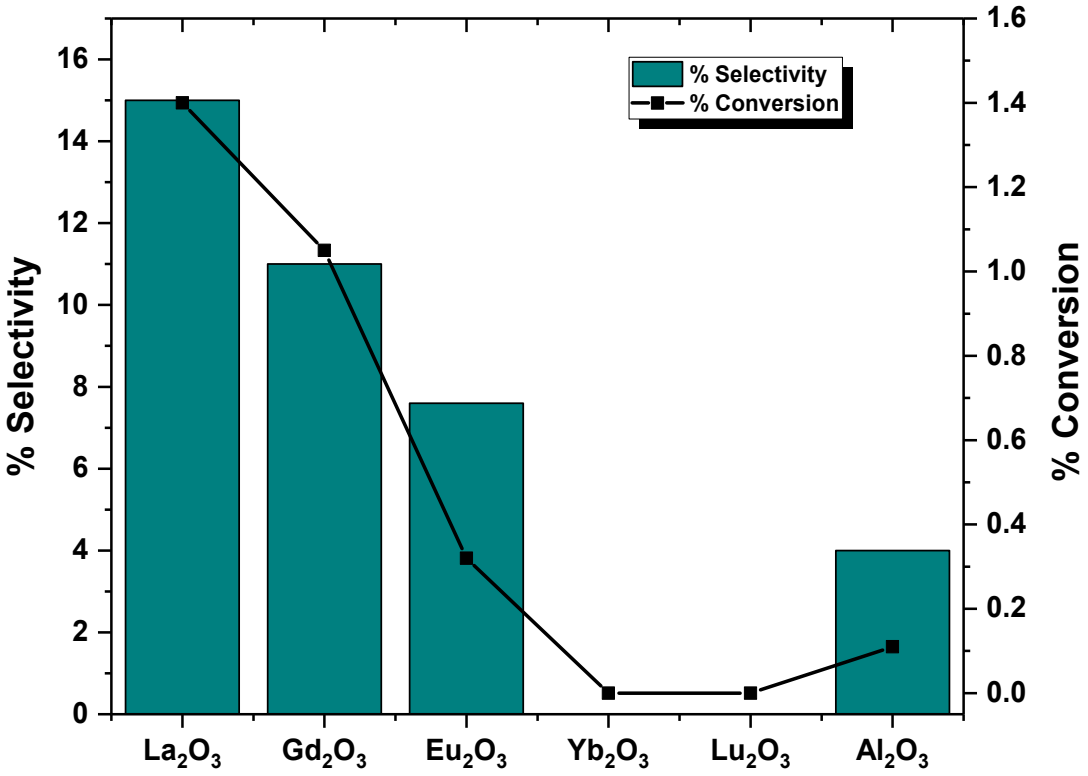

Figure S1 PO selectivity and conversion exhibited by Ln_2O_3 (Ln= La, Gd, Eu, Yb, Lu) and Al_2O_3-supported Ag nanospheres at 250 °C.

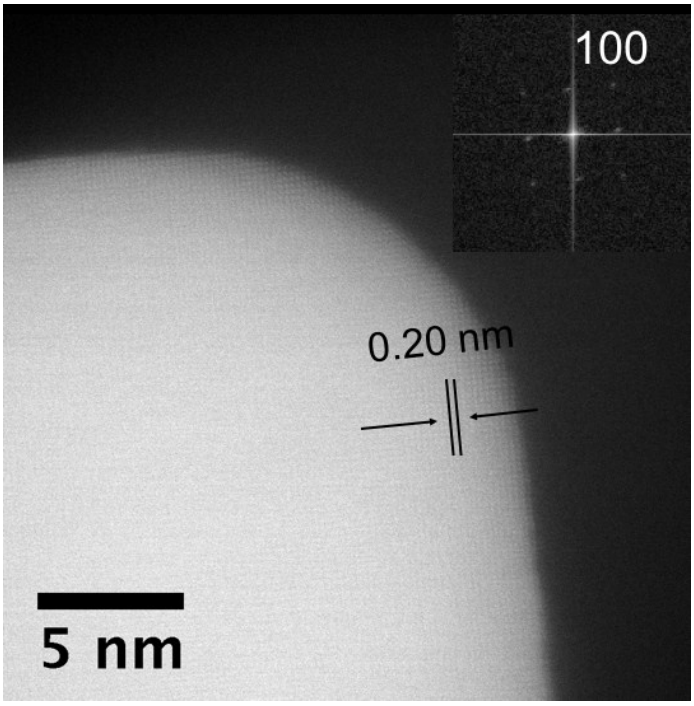

Figure S2 HAADF-STEM micrograph (dark field mode) of a Ag nanocube showing corresponding d-spacing: the inner image on top right-hand corner shows corresponding Fourier Transform (FT) pattern.

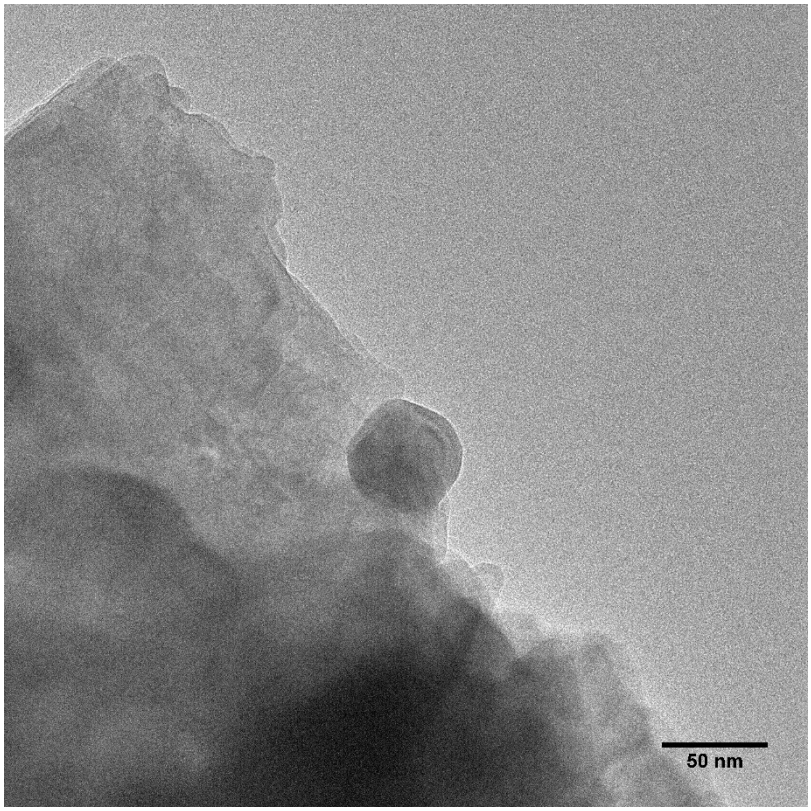

Figure S3 A typical TEM image of Ag nanocube/La_2O_3 catalyst after temperature programmed catalysis.

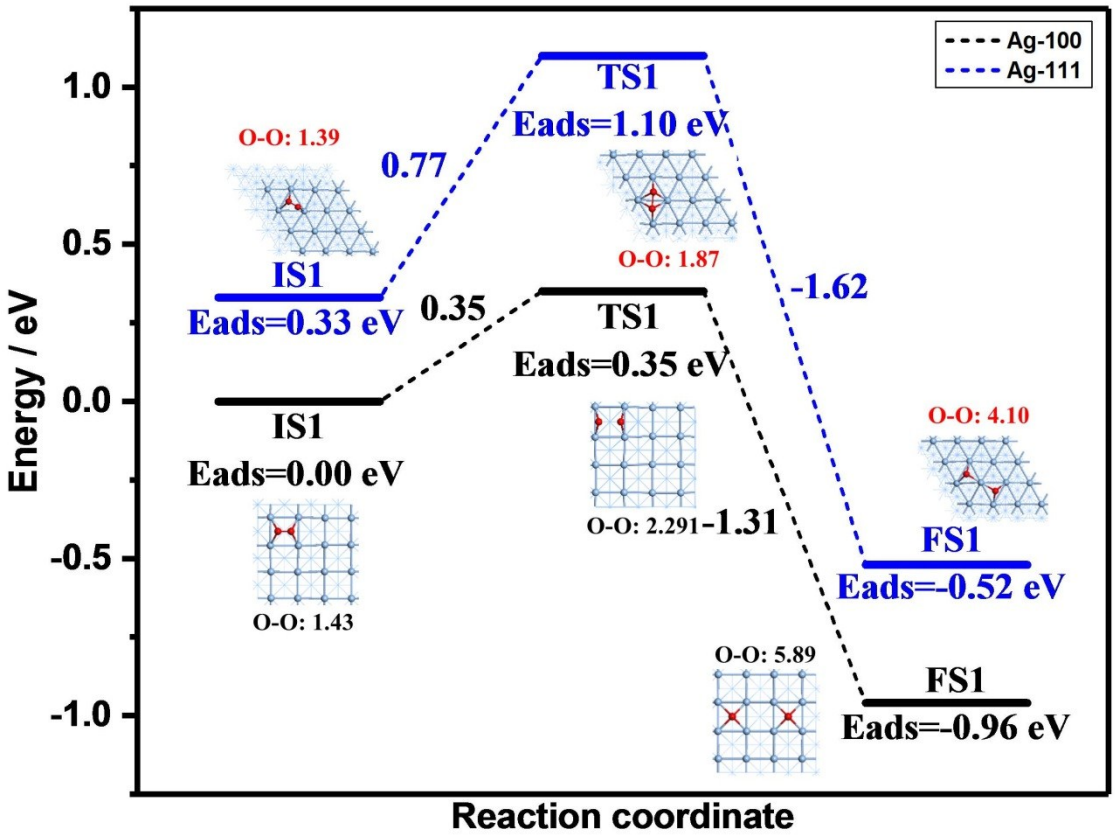

Figure S4. Energy diagram for oxygen dissociation on Ag(111) and Ag(100) surfaces.