

Influence of the Support on Propene Oxidation over Gold Catalysts

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Abstract: The epoxidation of propene without forming a substantial amount of byproducts is one of the holy grails of catalysis. Supported Cu, Ag and Au catalysts are studied for this reaction and the activity of the supported metals is generally well understood. On the contrary, limited information is available on the influence of the support on the epoxide selectivity. The reaction of propene with equal amounts of hydrogen and oxygen was tested over gold nanoparticles deposited onto CeO₂, TiO₂, WO₃, γ -Al₂O₃, SiO₂, TiO₂-SiO₂ and titanosilicate-1. Several metal oxide supports caused further conversion of the synthesized propene oxide. Strongly acidic supports, such as WO₃ and titanosilicate-1, catalyzed the isomerization of propene oxide towards propanal and acetone. Key factors for achieving high PO selectivity are having inert or neutralized surface sites, a low specific surface and/or a low density of surface -OH groups. This work provides insights and practical guidelines to which metal oxide support properties lead to which products in the reaction of propene in the presence of oxygen and hydrogen over supported gold catalysts.

Keywords: epoxidation; propene oxide; gold nanoparticles; support effects

S1. Mass titrations

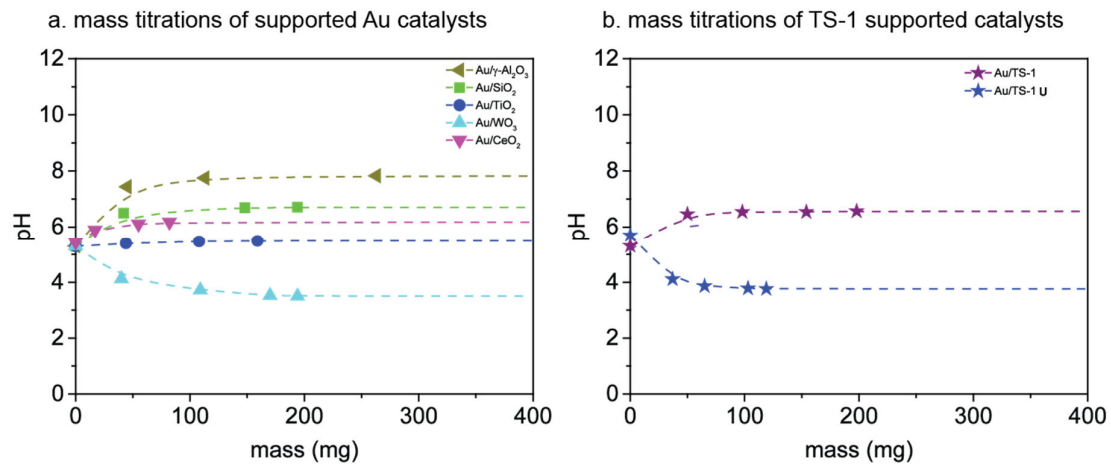


Figure S1. Point-of-zero-charge determinations of the supported Au catalysts using a 0.1 M KCl solution. Dashed lines were drawn to guide the eye.

S2. Additional TEM images

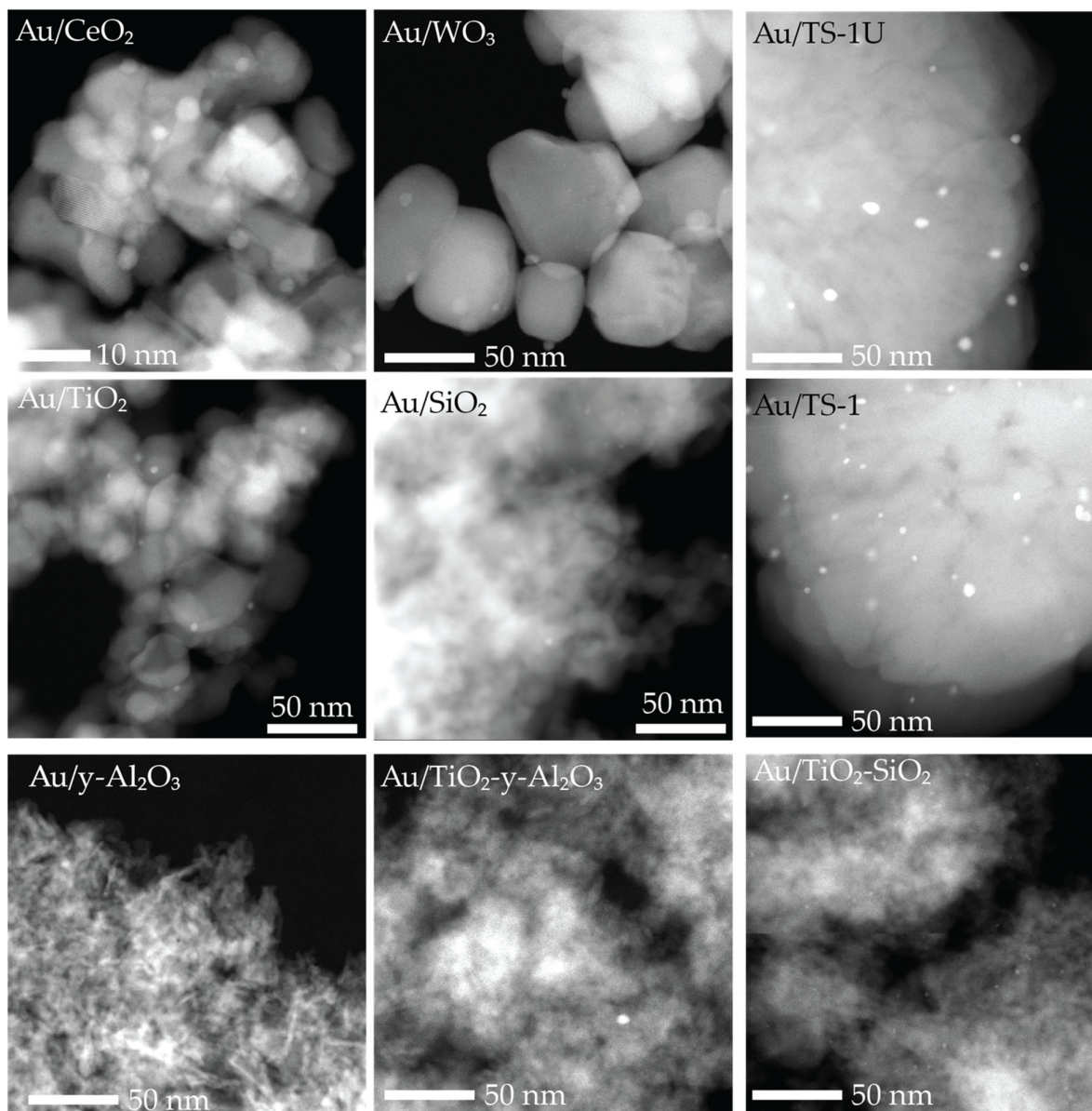


Figure S2. High Angle Annular Dark Field Scanning Transmission Electron Microscopy images of the indicated metal oxide supported gold catalysts.

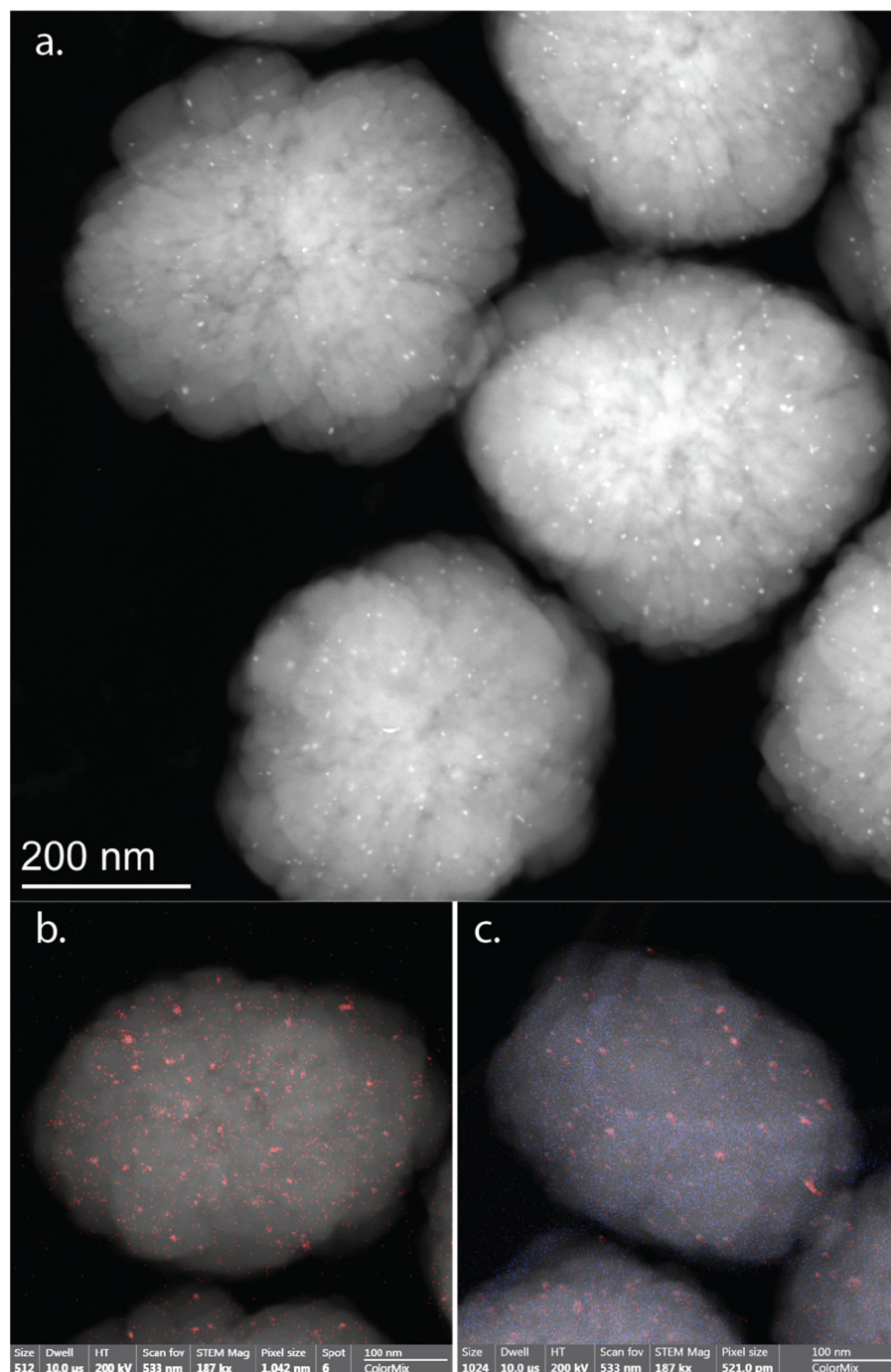


Figure S3. High Angle Annular Dark Field Scanning Transmission Electron Microscopy images of Au/TS1. (a). at low magnification, (b). energy dispersive X-ray spectroscopy (EDX) chemical map showing Au as the red dots, (c). EDX chemical map showing Au in red and Na in blue.

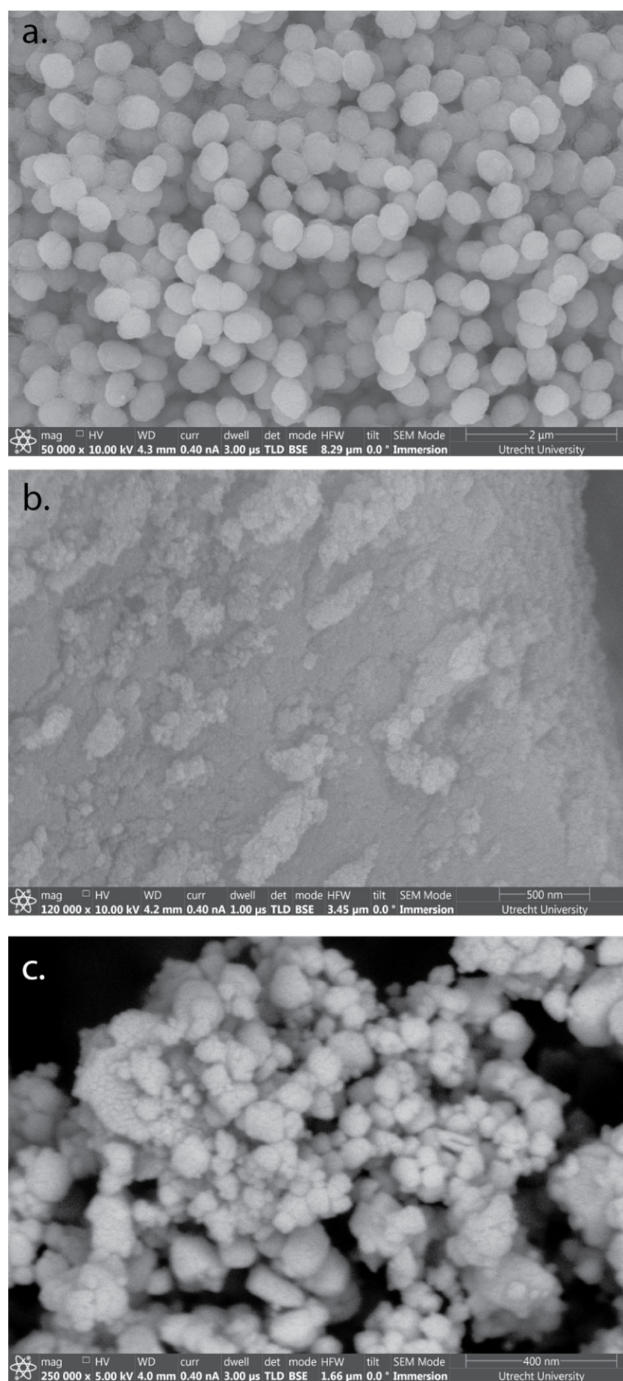


Figure S4. Scanning Electron Microscopy images of selected metal oxide supported gold catalysts (a). Au/TS-1, (b). Au/SiO₂, (c). Au/WO₃.

S3. Catalytic data

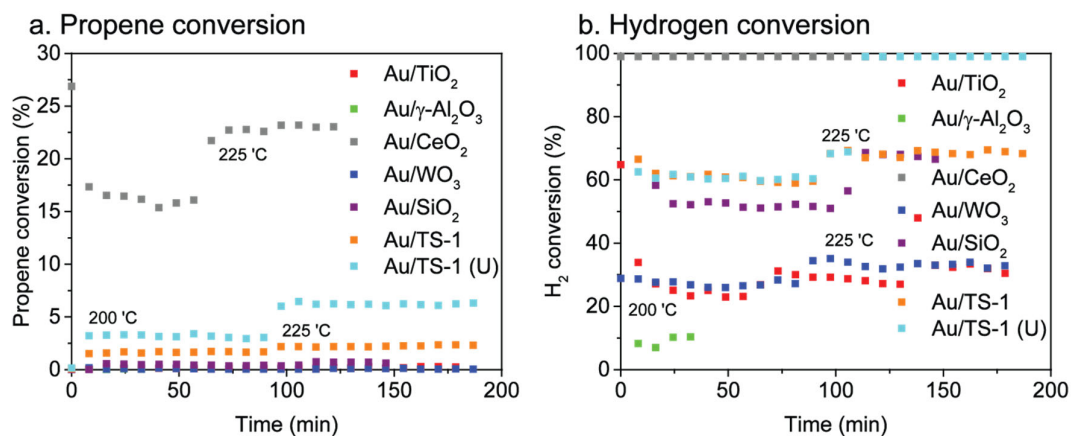


Figure S5. Conversion during propene (a) and hydrogen (b) oxidation over supported gold catalysts. Conditions: 150 mg of catalyst, 10,000 mL/g_{cat}/h flow of 10% of each C₃H₆, O₂ and H₂ in He at 200 °C-225 °C. 25 mg of Au/CeO₂ was used.

Table S1. Oxidation of propene at 200 °C in the presence of the supported gold catalysts^a.

| Catalyst | TOF (s ⁻¹) ^b | | Conversion (%) ^c | | Product selectivity (%) ^d | | | |
|--|-------------------------------------|----------------|-------------------------------|----------------|--------------------------------------|----------------------|-----------------------------|----------|
| | C ₃ H ₆ | H ₂ | C ₃ H ₆ | H ₂ | PO | Isomers ^e | Over-oxidation ^f | Acrolein |
| Au/CeO ₂ [†] | 0.28 | 1.28 | 17.4 | >99 | 0 | 0.2 | 99.8 | 0 |
| Au/WO ₃ | 0.01 | 1.40 | < 0.1 | 27.2 | 0 | 28.3 | 71.7 | 0 |
| Au/TiO ₂ | 0.01 | 3.10 | 0.2 | 34.8 | 21.8 | 21.7 | 56.5 | 0 |
| Au/SiO ₂ | 0.04 | 5.17 | 0.5 | 52.0 | 8.9 | 0 | 0 | 78 |
| Au/ γ -Al ₂ O ₃ | 0.01 | 0.03 | < 0.1 | 8.9 | 0 | 64.3 | 35.7 | 0 |
| Au/TS-1 | 0.07 | 2.38 | 1.7 | 60.5 | 88.9 | 9.1 | 2.1 | 0 |
| Au/TS-1U | 0.15 | 2.50 | 3.0 | 59.2 | 9.1 | 78.3 | 3.7 | 8.9 |
| Au/TiO ₂ - γ -Al ₂ O ₃ | n.d | n.d | 0.5 | 21.9 | 0 | 84.0 | 16.0 | 0 |
| Au/TiO ₂ -SiO ₂ | n.d | n.d | 3.6 | 78.8 | 76.6 | 0.3 | 10.1 | 13.0 |

^a Conditions: 150 mg of catalyst, 10,000 mL/g_{cat}/h flow of 10% of each C₃H₆, O₂ and H₂ in He at 200°C. ^b Turn-over frequency as molecule converted per surface Au atom. ^c Conversion averaged between 60-120 minutes of catalysis. ^d Selectivity averaged between 60-120 minutes of catalysis. ^e Propanal and acetone. ^f Acetaldehyde and CO₂ [†] Only 25 mg of catalyst was used.

Table S2. Comparison with Au catalysts that are used for gas phase propene oxidation in literature.

| Catalyst | Conditions ^a | X C ₃ H ₆ (%) ^b | PO | Major sideproducts (selectivity) | Reference |
|---------------------------------------|--|--|-----------------|--------------------------------------|-----------|
| | | | selectivity (%) | | |
| Au/CeO ₂ | 0.12% C ₃ H ₆ , 9% O ₂ , 294 °C ^c | 50 | 0 | CO ₂ (> 99%) | [1] |
| Au/CeO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^d | 17.4 | 0 | CO ₂ (> 99%) | This work |
| Au/Al ₂ O ₃ | 2.5% C ₃ H ₆ , 8.5% O ₂ , 275 °C ^e | n.m. | 0 | Mixture of oxygenates ⁱ | [2] |
| Au/Al ₂ O ₃ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | < 0.1 | 0 | Mixture of oxygenates ⁱ | This work |
| Au/SiO ₂ | 2.5% C ₃ H ₆ , 8.5% O ₂ , 262 °C ^g | n.m. | 0 | Acrolein (33%) + others ⁱ | [2] |
| Au/SiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 0.5 | 9 | Acrolein (78%) + others ⁱ | This work |
| Au/TiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 50 °C ^h | 1.1 | > 99 | - | [3] |
| Au/TiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 90 °C ^g | 0.5 | 20 | Mixture of oxygenates ⁱ | [4] |
| Au/TiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 0.2 | 22 | Mixture of oxygenates ⁱ | This work |
| Au/TS-1 | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^h | 0.6 | 4 | Propanal (74%) | [3] |
| Au/TS-1 | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ⁱ | 2.0 | 83 | Mixture of oxygenates ⁱ | [5] |
| Au/TS-1 | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 1.7 | 89 | Propanal, acetaldehyde | This work |
| Au/TS-1U | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 3.0 | 9 | Propanal (78%) | This work |
| Au/TiO ₂ -SiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 1.9 | 83 | CO ₂ (5%) | [6] |
| Au/TiO ₂ -SiO ₂ | 10% H ₂ , O ₂ , C ₃ H ₆ , 200 °C ^f | 3.6 | 77 | Mixture of oxygenates ⁱ | This work |
| Au/TiO ₂ -SiO ₂ | Promoted by Ba(NO ₃) ₂ and trimethylsilane 10% H ₂ , O ₂ , C ₃ H ₆ , <20 ppm NEt ₃ , 150 °C ^h | 8.5 | 91 | n.m. | [7] |

n.m.: not mentioned ^a Conditions: gas concentrations in an inert carrier gas (N₂, He or Ar) and temperature ^b conversion of propene. ^c GHSV 72,000 h⁻¹, ^d flow 60,000 mL/g_{cat}/h, ^e flow 311 mL/g_{cat}/h, ^f flow 10,000 mL/g_{cat}/h, ^g flow ca 2,300 mL/g_{cat}/h, ^h flow 4,000 mL/g_{cat}/h, ⁱ flow 6,600 mL/g_{cat}/h, ⁱ flow 14,000 mL/g_{cat}/h, ⁱ Mixture containing propanal, acetone, acetaldehyde, acrolein and/or CO₂.

S4. Deactivation of Au/TiO₂

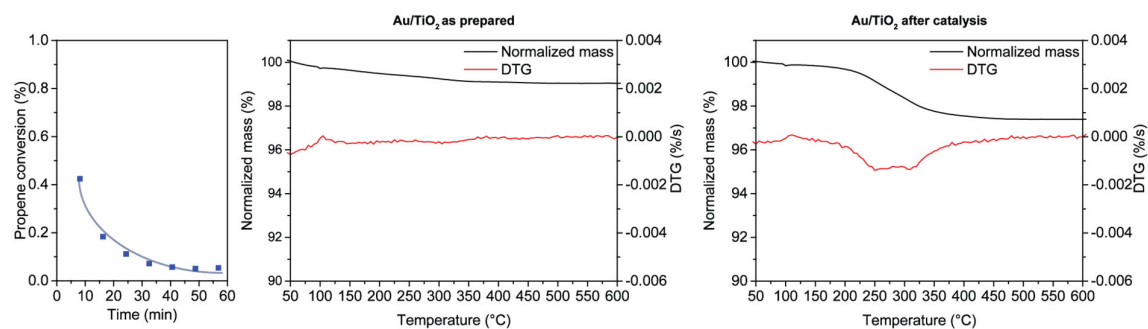


Figure S6. Au/TiO₂ catalyst in propene epoxidation propene conversion at 100 °C (a) and thermogravimetric analysis of the Au/TiO₂ before catalysis (b) and after the catalytic test (c).

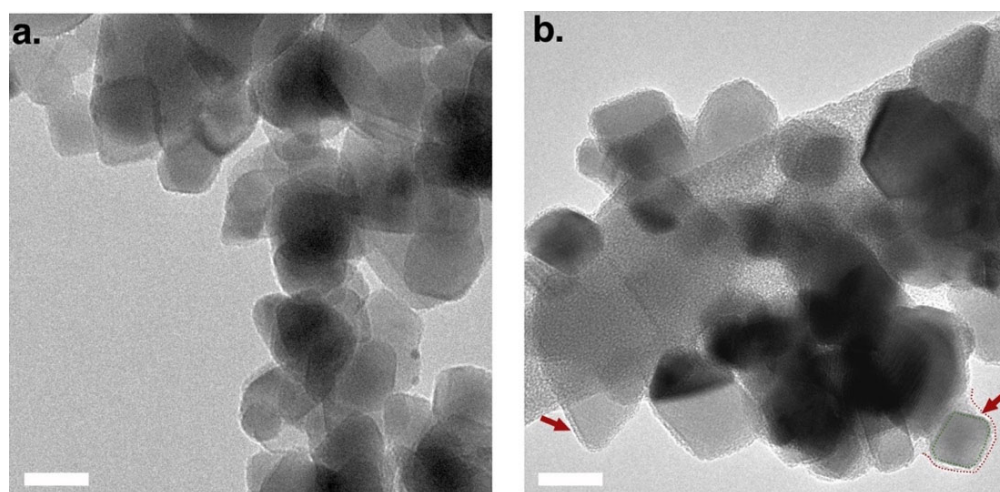


Figure S7. Representative Transmission Electron Microscopy micrographs of Au/TiO₂ before (a) and after catalytic propene epoxidation (b). The scalebar indicates 20 nm.

S5. N₂ Physisorption

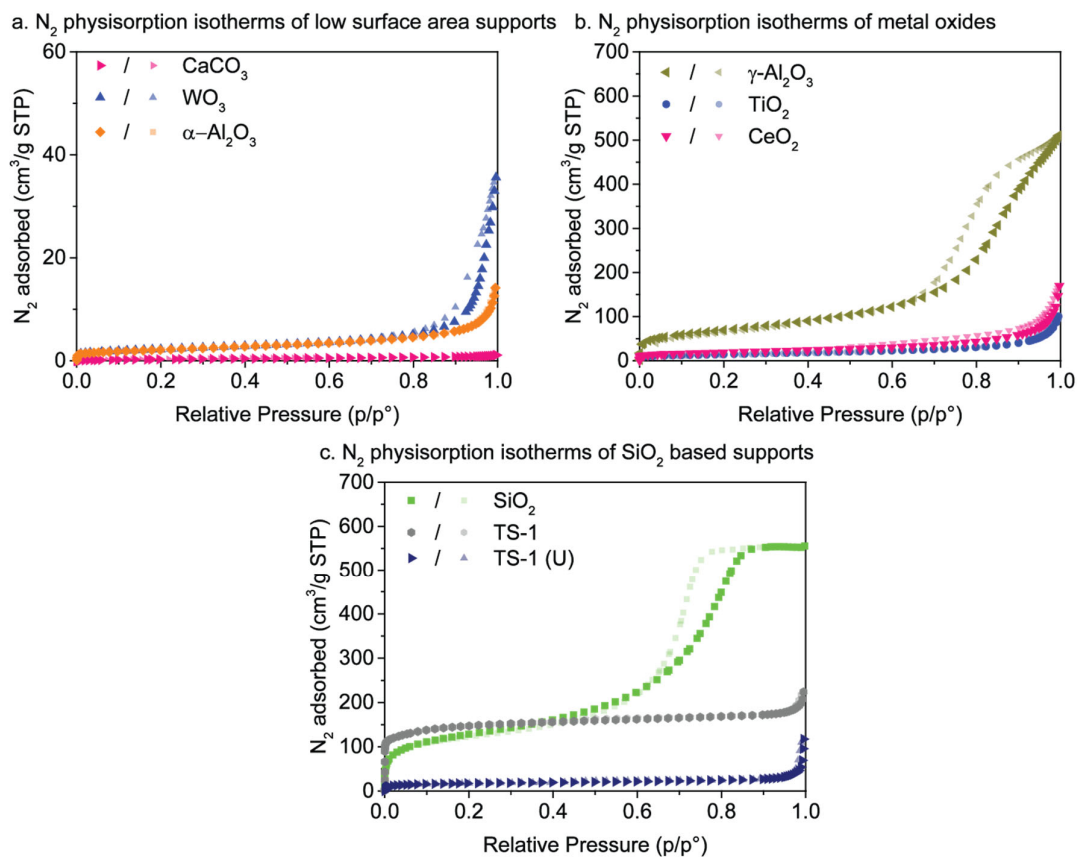


Figure S8. N₂ physisorption isotherms of the indicated metal oxide supports. The darker colored symbols represents the adsorption isotherm and faded symbols represent desorption isotherm. The TS-1U represents the TS-1 sample before a thermal decomposition step at 500 °C.

S6. FTIR with adsorption and desorption of Pyridine

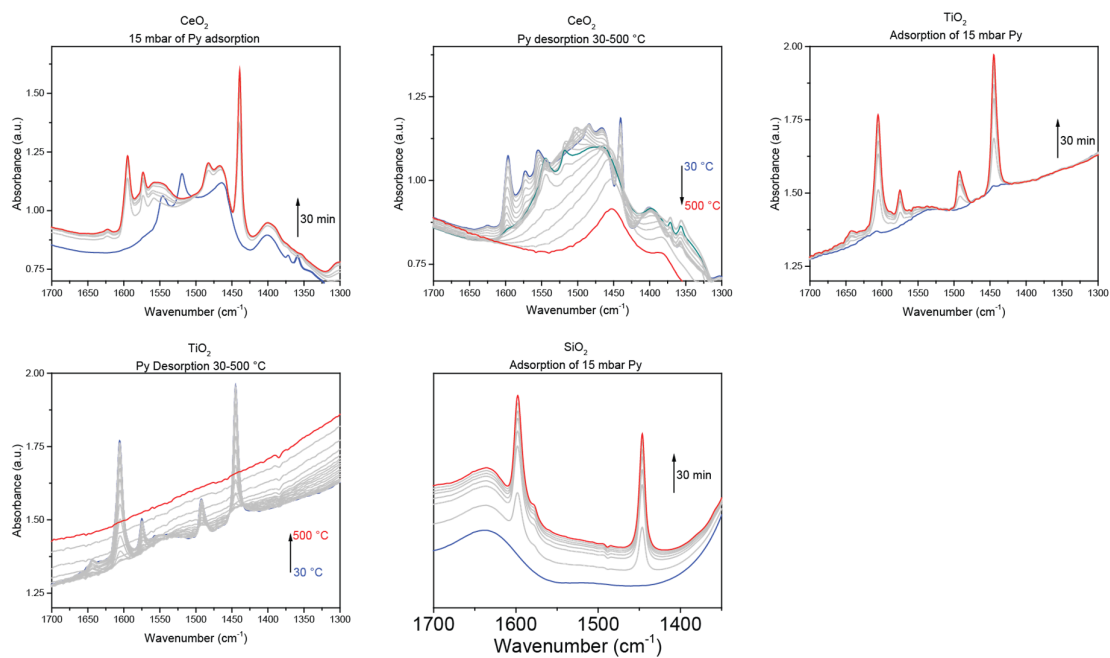


Figure S9. FTIR spectra of pyridine adsorption and desorption of the indicated oxide supports.

S7. NH₃-TPD

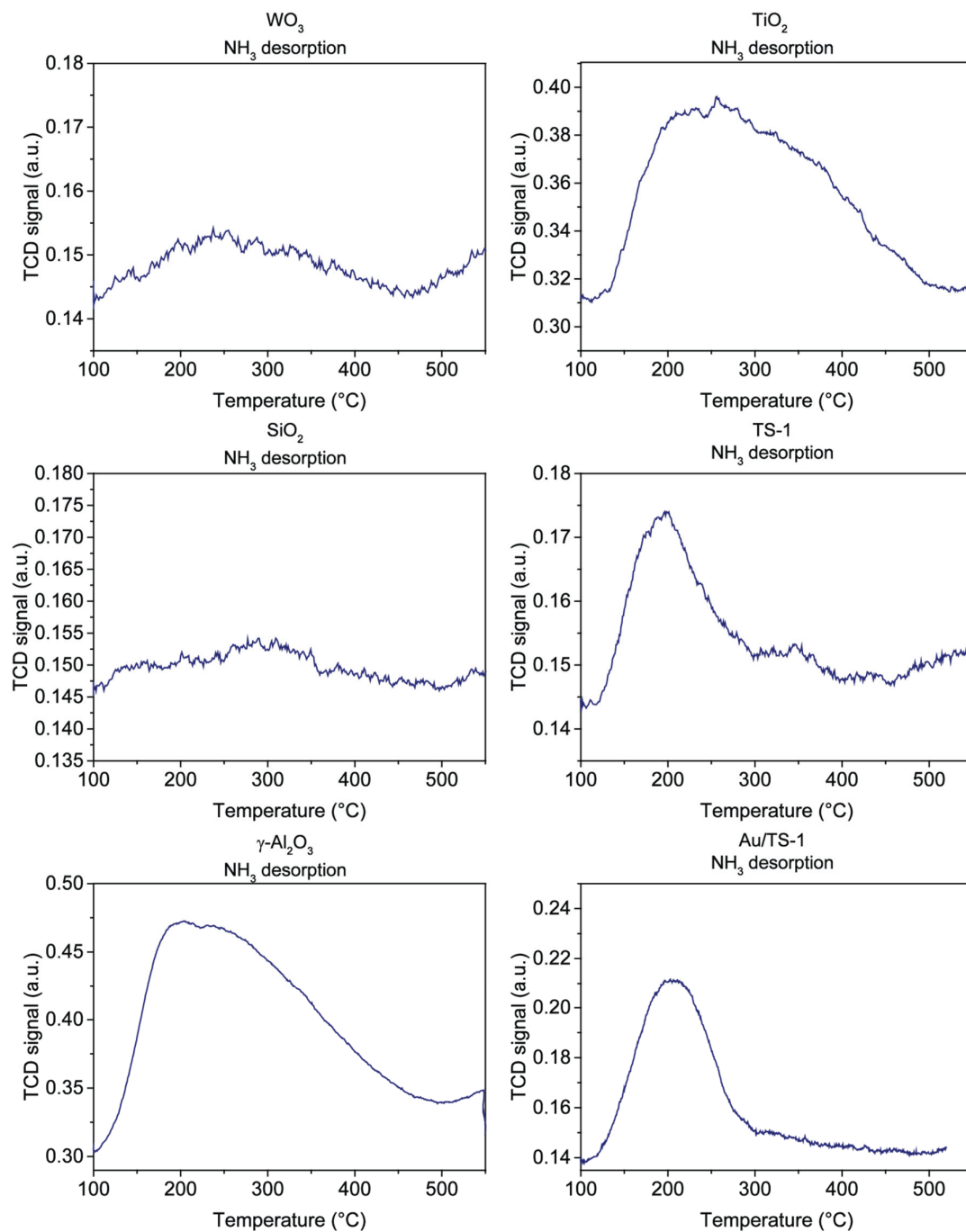


Figure S10. NH₃ temperature programmed desorption of the indicated oxide supports.

S8. Diffuse Reflectance UV-Vis

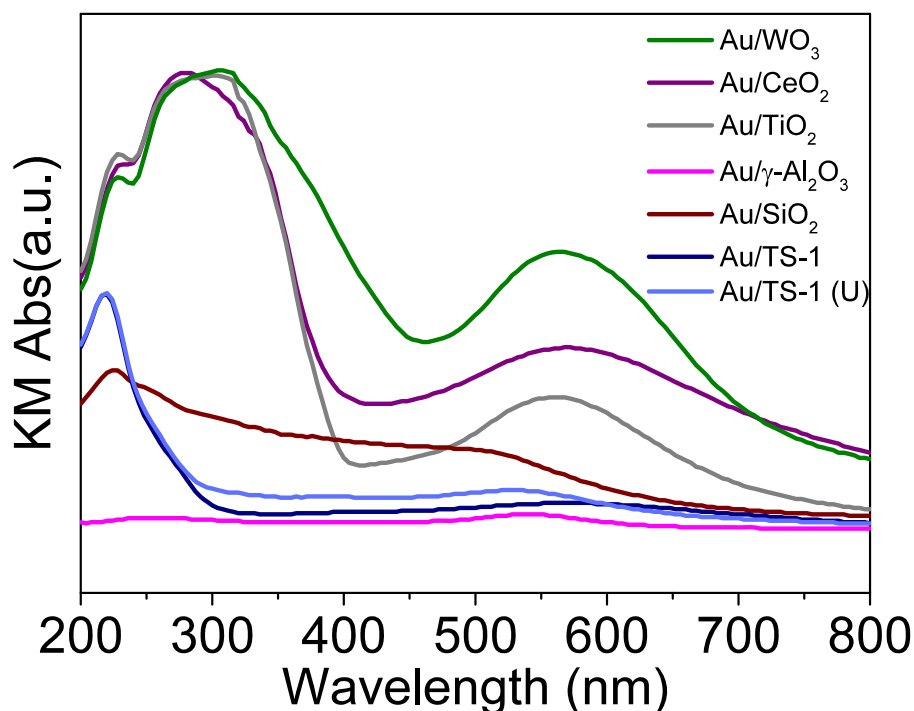


Figure S11. Diffuse Reflectance UV-Vis absorbance spectra of the supported Au catalysts.

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