

Electronic Supplementary Information

A Novel and Simple Method Yields High-Dispersed Au/TS-1 Catalysts for Enhanced Propylene Hydro-Oxidation

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1 Catalysts preparation

1.1 Synthesis of titaniumsilicate-1

The TS-1 with a Si/Ti molar ratio of 200 was synthesized as follows: 2.00 g of Tween-20 was firstly added to a beaker containing 30.00 g of H₂O and stirred magnetically for 1 h at room temperature. Subsequently, 26.36 g of tetrapropylammonium hydroxide (TPAOH, 25 wt%) was added into the above solution and stirred for another 1 h. Following this, 37.5 g of tetraethyl orthosilicate (TEOS, 99.8%) was introduced and stirred for 1 h. Concurrently, 0.31 g of titanium butoxide (TBOT, 99.99) was dispersed in 10 g isopropanol (IPA, 99.5%) and stirred magnetically for 45 minutes. Thereafter, the TBOT and IPA mixture was added dropwise into the above-mentioned mixture using a syringe pump. After stirring at room temperature for 1 h, the resulting gel is then heated to 80°C to remove alcohol. After the alcohol evaporation process, the gel was then transferred into a Teflon-lined stainless-steel autoclave (150 ml), which was then crystallized at 165°C for 24 h. The as-synthesized TS-1 After the crystallization process, the resulting slurry was centrifuged and washed. Then the obtained sample was dried at 70°C for 6 h in a convection oven. Finally, the as-obtained solid was placed in a muffle furnace and calcined at 550 °C for 5 h in air. For the uncalcined TS-1 (i.e., TS-1-B) with a Si/Ti ratio of 100, the synthesis process is similar to that of the TS-1(200), with the key difference being the absent of calcination process.

1.2 Synthesis of catalysts

The process for preparing Au/TS-1 catalyst by the modified incipient wetness impregnation method (denoted as m-IWI) was as follows: 0.500 g of TS-1(200) was firstly placed in a PTFE crucible, then 0.200 mL of HAuCl₄ (12.70 mM) solution was added dropwise into the TS-1 solid, and 0.200 mL of Cs₂CO₃ (0.05 M) solution was subsequently introduced into the above

slurry by stirring. The impregnated solid powder was aged at room temperature for 6 h and then placed into a dark vacuum dryer for 12 h at room temperature. The as-obtained sample was denoted as x wt% Au/TS-1(m-IWI), where x represents the Au loading. The uncalcined TS-1 immobilized Au catalyst was also prepared via the similar method mentioned above, except for the usage of 0.125 mL of Cs₂CO₃ solution. The as-obtained sample was denoted as x wt% Au/TS-1-B(m-IWI), where x represents the Au loading. The referenced Au/TS-1 catalyst using HAuCl₄ as Au precursor was also prepared via the similar method mentioned above, except for the addition of Cs₂CO₃ solution. The as-obtained sample was denoted as x wt% Au/TS-1(IWI), where x represents the Au loading.

The deposition-precipitation method (i.e., DP method) was also used to prepare referenced Au/TS-1 catalyst. Typically, 0.50 g of TS-1 powder was dispersed in 22.0 g ultrapure H₂O, followed by the addition of 2.50 mL of HAuCl₄ solution (4.80 mM). After stirring for 0.5 h at room temperature, 0.36 ml of Cs₂CO₃ (1.00 M) solution was added into the above slurry. After aging at room temperature for 5 h, the obtained slurry was centrifuged, washed, and dried for 18 h under vacuum. The as-obtained sample was denoted as x wt% Au/TS-1(DP), where x represents the Au loading.

2 Characterization

The Fourier-transform infrared spectroscopy (FT-IR) spectra of the three catalysts prepared by different methods were collected on a PerkinElmer Spectrum 100 FT-IR spectrometer. Prior to analysis, samples were first mixed with KBr and then pressed into pellets. The electronic properties of Au/TS-1 catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis XSAM-800 instrument, which employed Al K α X-ray (1486.6 eV) as the excitation source. The internal standard of the C_{1s} peak was set as 284.6 eV. The Au loadings of Au-Ti

bifunctional catalysts were determined using an Agilent 725 inductively coupled plasma atomic emission spectrometer (ICP-AES). Prior to analysis, the samples were fully digested in a mixture of aqua regia and hydrofluoric acid. The images of Au particle over the Au-Ti bifunctional catalysts were obtained using a high-angle annular dark field-scanning transmission electron microscope (HAADF-STEM), which was performed on FEI Tecnai G2 F20 S-TWIN transmission electron microscope. The average Au particles size and the size distribution of Au nanoparticles over the Au-Ti bifunctional catalysts were obtained based on at least 200 randomly selected Au nano-particles. The Aberration-corrected high-angle annular dark-field scanning transmission electron microscope was performed on FEI Titan Cubed Themis G2 300 with a spherical aberration corrector working at 200 kV.

3 Catalytic tests

Catalytic testing was conducted in a quartz tubular reactor (inner diameter of ~ 6 mm) at normal pressure. For the TS-1 immobilized Au catalysts (e.g., Au/TS-1(m-IWI), Au/TS-1(DP)), 0.15 g catalyst of 100 mesh size was loaded in the reactor. Subsequently, the reactor was heated from room temperature to 190 °C (0.5°C/min) in a gas mixture of C₃H₆: O₂: H₂: N₂ =1:1:1:7 (flow rate of 35 mL·min⁻¹) and then kept at 190 °C for catalytic testing. The Au/TS-1-B (m-IWI) catalyst was pre-treated prior to the propylene epoxidation. Typically, 0.15 g Au/TS-1-B(m-IWI) catalyst of 100 mesh size was firstly loaded in the reactor, and then the reactor was heated from room temperature to 350 °C (heating rate of 1 °C /min) in a feed of H₂/N₂ mixture with the flow rate of 18/32 mL/min and kept for 2 h. Subsequently, the reactor was cooled down to 200 °C and the feed gases were switched to C₃H₆/H₂/O₂/N₂ with the flow rate of 3.5/3.5/3.5/24.5 mL/min for the catalytic testing.

The reactor gas effluent was analyzed hourly by using an on-line GC equipped with TCD (TDX-01 column) and FID (Rt-QS-BOND column), which uses N₂ as the carrier gas. The

propylene, ethanal, PO, acetone, acrolein and propanal were analyzed by FID, and the H₂, O₂ and CO₂ were detected by TCD. The conversion of propylene, selectivity toward products and H₂ efficiency were calculated as below:

Propylene conversion = moles of (C₃-oxygenates + 2/3 ethanal + 1/3 CO₂)/moles of propylene in the feed.

C₃-oxygenates selectivity = moles of C₃-oxygenates/moles of (C₃-oxygenates + 2/3 ethanal + 1/3 CO₂).

Ethanal selectivity = 2/3 (moles of ethanal)/moles of (C₃-oxygenates + 2/3 ethanal + 1/3 CO₂).

CO₂ selectivity = 1/3 (moles of CO₂)/moles of (C₃-oxygenates + 2/3 ethanal + 1/3 CO₂).

H₂ efficiency = moles of PO/moles of H₂ converted.

Table S1. Au loadings and uptake efficiency of Au/TS-1 catalysts prepared by different methods

Catalysts	Theoretical	Practical	Au uptake efficiency (%)
	Au loading (wt%)	Au loading (wt%)	
Au/TS-1(m-IWI)	0.10	0.098	98.0
Au/TS-1(IWI)	0.10	0.097	97.0
Au/TS-1(DP)	4.75	0.093	2.2

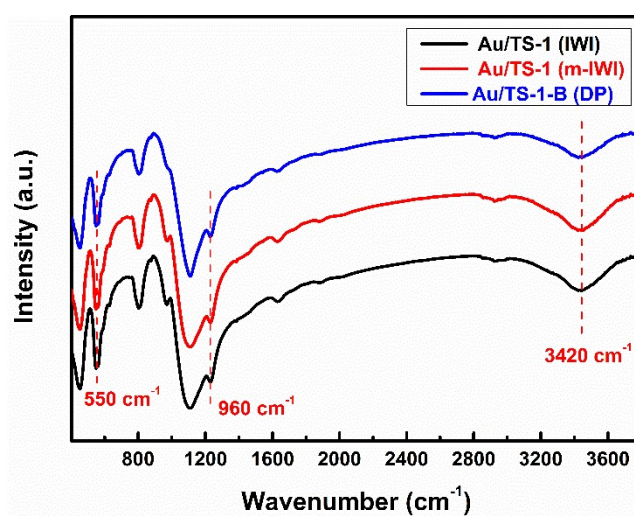


Fig. S1. FT-IR spectra of three Au/TS-1 catalysts prepared by different methods.

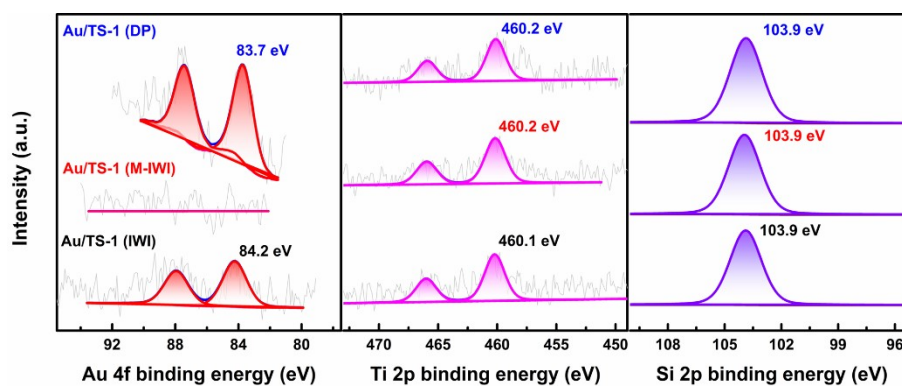


Fig. S2. XPS spectra of Au/TS-1 catalysts prepared by different methods.

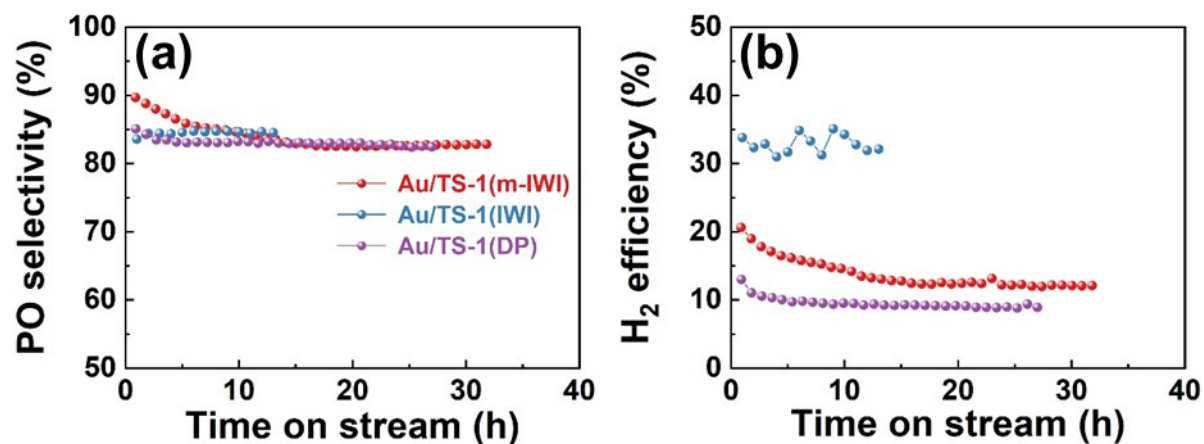


Fig. S3 (a) PO selectivity and (b) hydrogen efficiency of the 0.10 wt% Au/TS-1 catalysts prepared by different methods.

Reaction temperature: 190 °C, C₃H₆ concentration: 10% Vol.

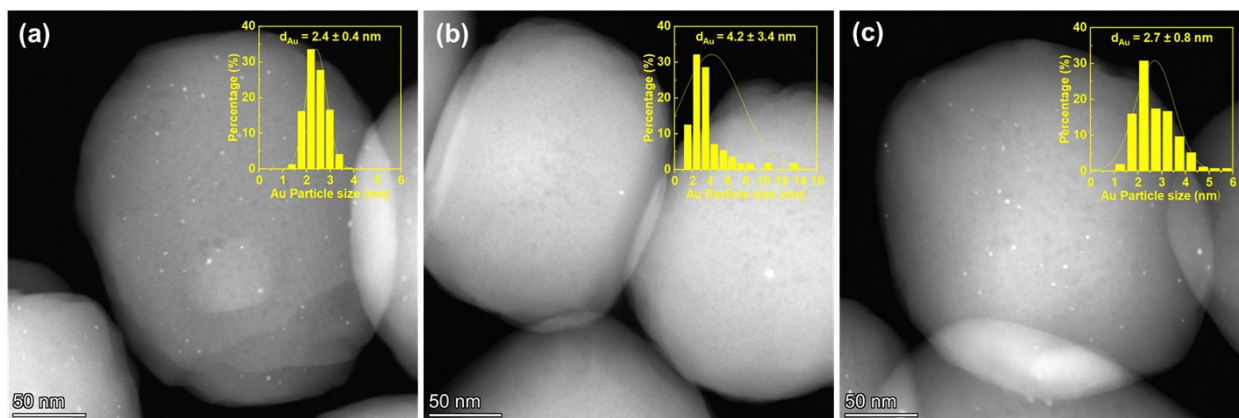


Fig. S4 Representative HAADF-STEM images of (a) 0.10 wt.% Au/TS-1(m-IWI), (b) 0.10 wt.% Au/TS-1(IWI) and (c) 0.10 wt.% Au/TS-1(DP) catalysts. The insets show the Au nanoparticle size distributions of the corresponding catalysts.

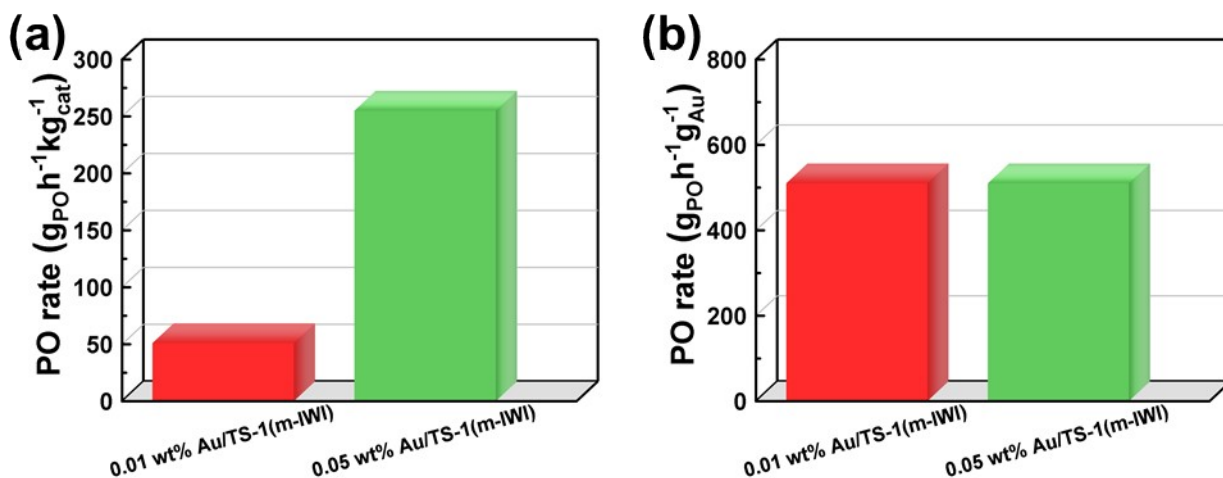


Fig. S5 (a) PO formation rate and (b) gold atom efficiency of the 0.01 wt% Au/TS-1(m-IWI) and 0.05 wt% Au/TS-1(m-IWI) catalysts. Reaction temperature: 190 °C, C_3H_6 concentration: 10% Vol.

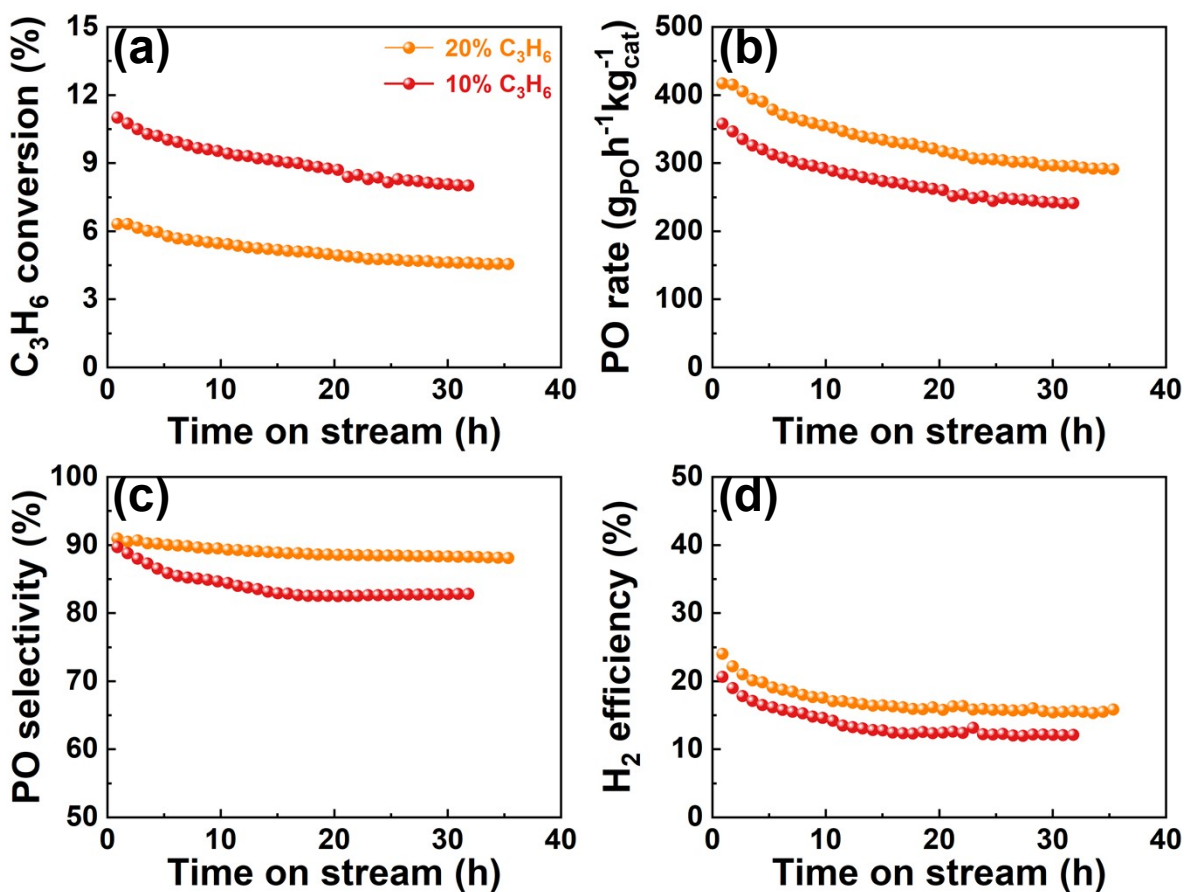


Fig. S6 (a) Conversion of propylene, (b) PO formation rate, (c) PO selectivity and (d) hydrogen efficiency of 0.10 wt.% Au/TS-1(m-IWI) catalyst under different C_3H_6 concentrations. Reaction temperature: 190 °C.

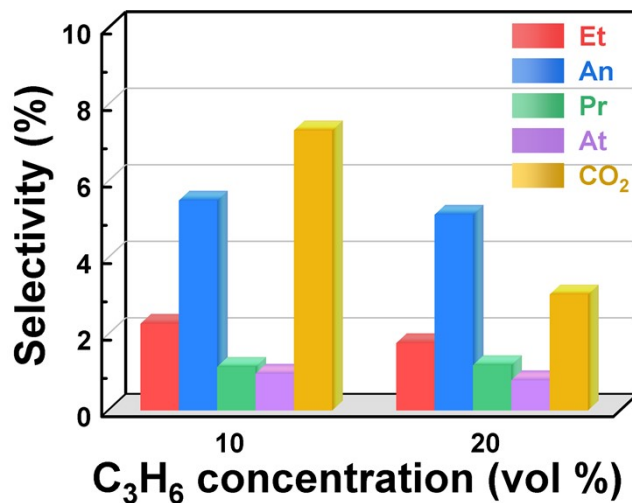


Fig. S7 Comparison of byproducts distribution of 0.10 wt.% Au/TS-1(m-IWI) catalyst under different C₃H₆ concentrations. Reaction temperature: 190 °C.

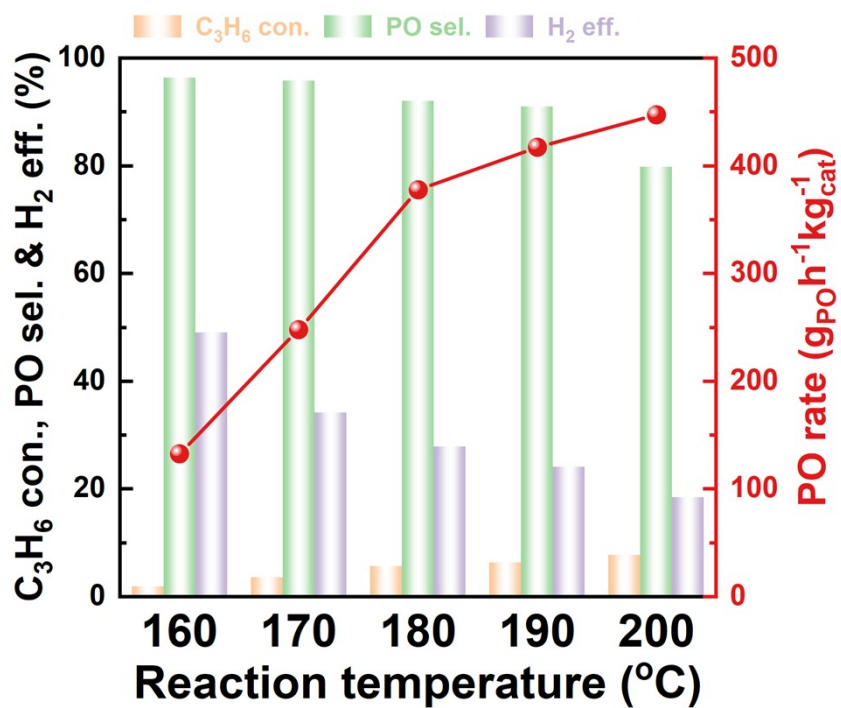


Fig. S8 Effect of reaction temperature on the catalytic performance of 0.10 wt.% Au/TS-1 0(m-IWI) catalyst. C₃H₆ concentration: 20% Vol.

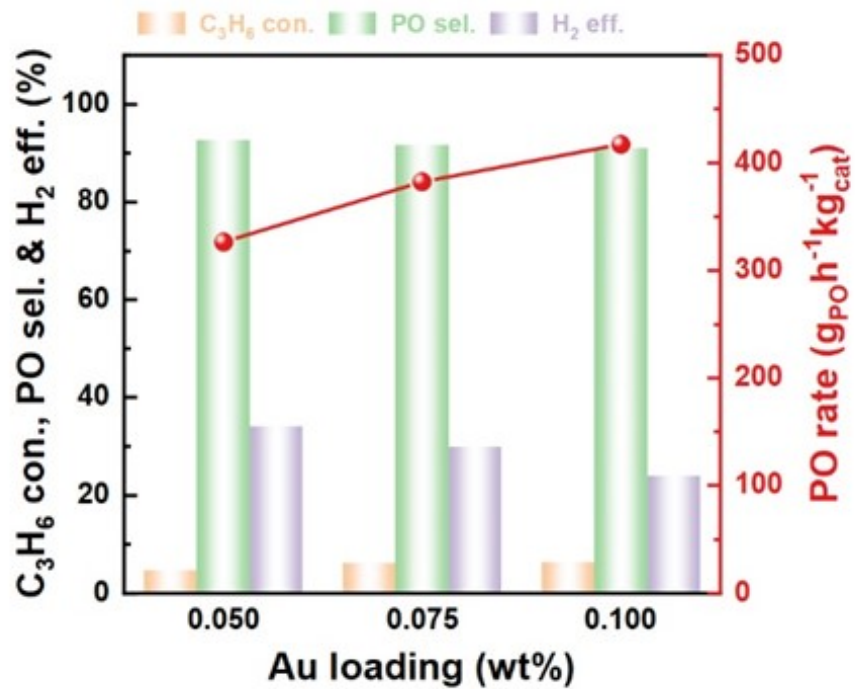


Fig. S9 Effect of Au loading on the catalytic performance of Au/TS-1(m-IWI) catalysts. Reaction temperature: 190 °C, C₃H₆ concentration: 20% Vol.

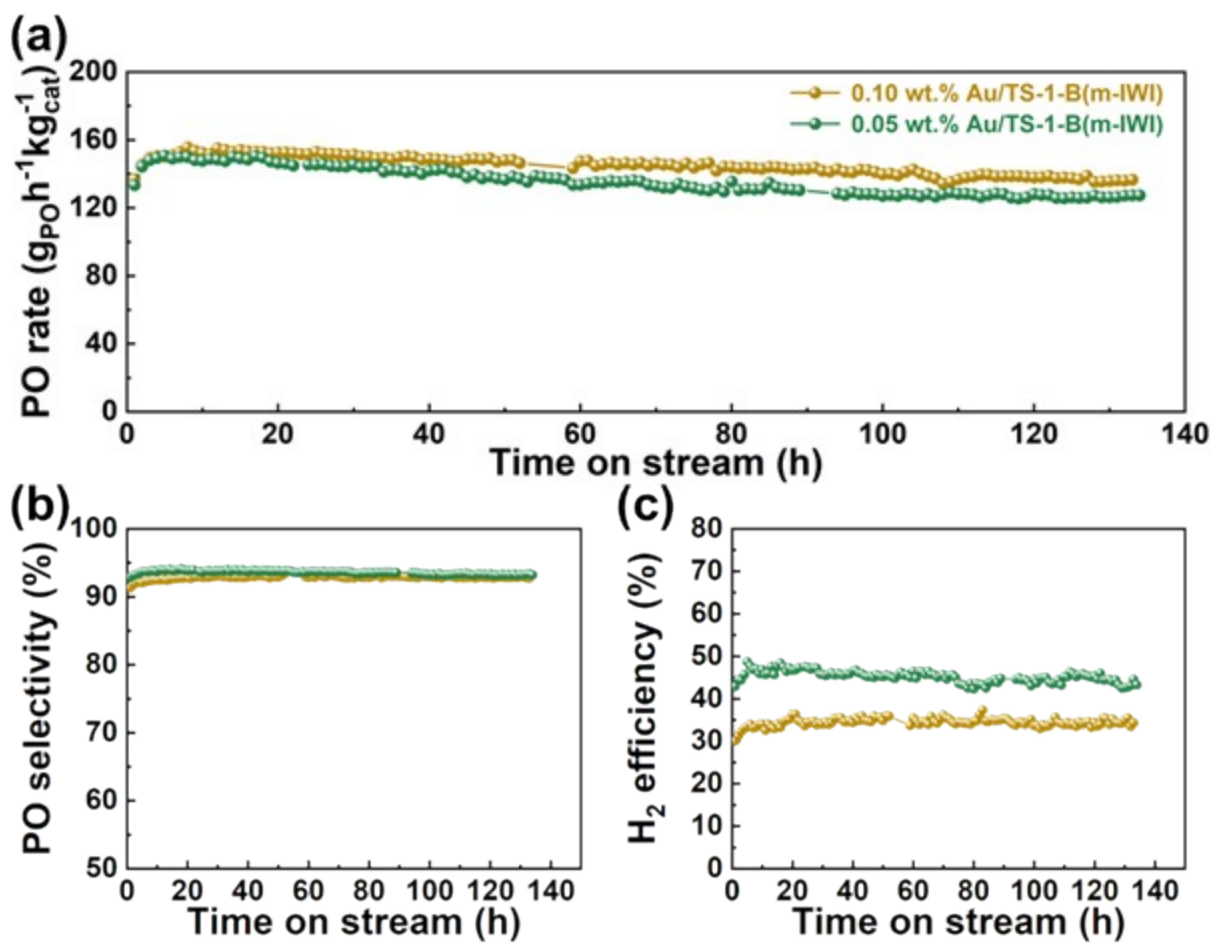


Fig. S10 The PO formation rate (a) and selectivity (b), as well as hydrogen efficiency (c) of the Au/TS-1-B(m-IWI) catalyst with different Au loadings. Reaction temperature: 200 °C, C_3H_6 concentration: 10% Vol.

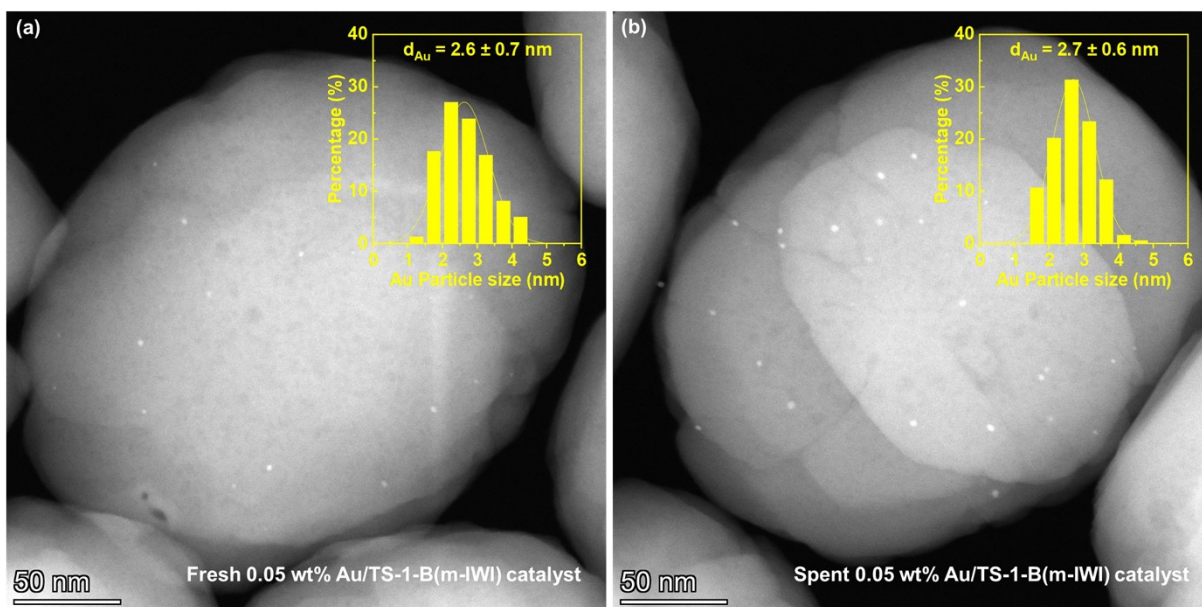


Fig. S11 Representative HAADF-STEM images of fresh and spent 0.05 wt% Au/TS-1-B(m-IWI) catalyst. The insets show the Au nanoparticle size distributions of the corresponding catalysts.