Pollen-Templated Bio-TS-1: A Sustainable Catalyst with Hierarchical Porosity for Propylene Epoxidation

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Experimental section

Chemical and Materials

The following chemicals were used without further purification. Rape pollens were obtained from WuTaishan Bee Industry Co., Ltd. (China). Tween 20 and tetrapropyl ammonium hydroxide (TPAOH, 40%) was purchased from Aladdin Chemicals Co. Ltd. Tetraethyl orthosilicate (TEOS, 98%), tetrabutyl titanate (TBOT), isopropyl alcohol (IPA, 99%), Chloroauric acid (HAuCl₄·4H₂O, 99.9%) and Urea (CO(NH₂)₂, 99%) was bought from Sinopharm Chemical Reagent Co. Ltd., China.

Characterizations

X-ray diffraction (XRD) was performed using an Ultima IV (Rigaku, Japan) with Cu K α radiation, scanning from 5 to 60° at a rate of 10°/min. The Fourier transform infrared (FTIR) spectra were collected using a Nicolet N6700 spectrometer (Thermo, USA) with a resolution of 4 cm⁻¹. The diffuse reflectance ultraviolet-visible spectra (DR-UV vis) were measured in a range of 200-800 nm with a Cary-5000 spectrometer (Varian, USA) using BaSO₄ as a reference. The UV-Raman spectroscopy was performed using a Horiba LabRAM HR Evolution instrument equipped with a 325 nm laser. The elemental composition was determined using an Agilent 730 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). N₂ adsorption-desorption isotherms were carried out using a porosimetry apparatus at 77 K (Micromeritics ASAP 2460, USA) to obtain the surface area and pore size distribution of the sample. The size and morphology of the sample were observed using scanning electron microscope (SEM) system (ZEISS SIGMA, Germany) with an energy beam of 10.0 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250 XPS system (Thermo, USA) equipped with an Al Ka X-ray source in which all the binding energies were calibrated with C 1s at 284.8 eV. The Raman spectra were characterized employing an in Via spectroscope (Renishaw, UK), in which the samples were exposed to the laser output (He-Ne light at 532 nm, 100%) at various exposure times. During Raman testing, Ti-OOH species were created by mixing 0.1 g of zeolite with 50 μ L of 30% hydrogen peroxide aqueous solution and then grinding it well. *In situ* DRIFTS of PO were carried out using a Nicolet N6700 spectrometer (Thermo, USA) with a transmission cell using CaF₂ windows. The sample powder was loaded into the cuvette, treated with N₂ at 200 °C for 1 h, cooled to room temperature and then the spectra were recorded in a N₂ environment. The adsorption process was observed by passing PO at the reaction temperature, and the spectra were recorded every 1 min.

Catalyst Evaluation

The catalytic reaction was conducted in a fixed packed-bed reactor at a temperature of 200 °C without any pre-treatment. The feed gas, composed of 10% C_3H_6 , 10% H_2 , 10% O_2 , and 70% Ar, was introduced into the reactor at a gas hourly space velocity (GHSV) of 14,000 mL g_{cat.}⁻¹ h⁻¹. The catalysis properties were assessed in a fixed-bed reactor with two sets of gas chromatograph (GC9560, China), using N₂ and Ar as carrier gas. The residual content of H₂ and propylene was analyzed using the thermal conductivity detector (5A packed column, 2 mm·4 m, 0.15 MPa, 150 °C, Huaai. Inc.). The products containing acetaldehyde (Et), propylene oxide (PO), propane (Pr), acetone (An), and acrolein (Ac) along with the remaining propylene were detected by the flame ionization detector (FFAP capillary column, 0.53 mm·50 m, 0.04 MPa, 60 °C, APPARATUS, Inc.). Furthermore, the catalytic performances were calculated based on the equations below.

 $\operatorname{Conversion of C_{3}H_{6}} = \frac{\operatorname{mol of (C3H6)_{in} - mol of (C3H6)_{out}}}{\operatorname{mol of (C3H6)_{out}}}$ $\operatorname{Selectivity of PO} = \overline{\operatorname{mol of (PO)}}$ $\operatorname{Mol of (PO)}$ $\operatorname{H_{2} efficiency} = \overline{\operatorname{mol of (H2)_{in} - mol of (H2)_{out}}}$

Sa	ample	$\mathrm{S}_{\mathrm{BET}}^{\mathrm{a}}$ $(\mathrm{m}^2~\mathrm{g}^{-1})$	S_{micro}^{b} $(m^2 g^{-1})$	V _{total} ^c (cm ³ g ⁻¹)	V_{meso}^{d} (cm ³ g ⁻¹)	Ti Element content ^e (wt. %)
	TS-1	421	272	0.44	0.27	3.0
bi	o-TS-1	414	241	0.67	0.52	2.8

Table S1. The physical properties of TS-1 and bio-TS-1

 $^{\mathrm{a}}$ The S_{BET} was calculated according to the BET model.

^b The Smicro was obtained from the t-plot analysis.

 $^{\rm c}$ The V_{total} was determined from the adsorption amount at a relative pressure of 0.99.

 $^{\rm d}$ The $V_{\rm meso}$ was calculated using the BJH adsorption branch.

^e The Ti content measured with the ICP-OES.



Figure S1. The XRD patterns for Au/bio-TS-1 and Au/TS-1 samples.



Figure S2. The UV-Raman spectra for bio-TS-1 and TS-1 samples.



Figure S3. The DR-UV spectra for Au/bio-TS-1 and Au/TS-1 samples.



Figure S4. The XPS spectra for Au 4f of Au/bio-TS-1 and Au/TS-1 samples.



Figure S5. Raman spectra of bio-TS-1 and bio-TS-1+HOOH.



Figure S6. The intensity of quasi in situ Raman spectra at 637 cm⁻¹.



Figure S7. H₂O yield of Au/bio-TS-1 and Au/TS-1 catalyst.