

Supporting Information

Fabrication of Silver-Tungsten Wafer-like Nanoarchitectures for Selective Epoxidation of Alkenes

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DETAILED CHARACTERIZATION TECHNIQUES

- 1. X-ray power diffraction (XRD).** Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K α radiation source. Diffraction patterns in the 2°-80° region were recorded at a rate of 0.5 degrees (2 θ) per minute.
- 2. Scanning electron microscopy (SEM).** Scanning electron microscopy images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanumhexaboride (LaB $_6$) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer.
- 3. Transmission electron microscopy (TEM).** TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid.
- 4. X-ray photoelectron spectroscopy (XPS).** X-Ray photoelectron spectra were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies (± 0.1 eV) were determined with respect to the position C 1s peak at 284.8 eV.
- 5. Raman spectroscopy.** Raman spectra were measured by a microscopic Raman spectroscopic system, Renishaw Ramascope, excited with a He-Ne Laser at 633 nm.

6. Extended X-ray absorption fine structure spectroscopy (EXAFS). Measurements of extended X-ray absorption fine structure (EXAFS) at Ag-K edge were carried out in a transmission mode at room temperature at the NW10A station of the Photon Factory-Advanced Ring for pulse X-Rays at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF-AR). The electron storage ring was operated at 6.5 GeV. Synchrotron radiation from the storage ring was monochromatized by a Si (311) channel cut crystal at Ag K-edge. Ionization chambers, which were used as detectors for incident X-ray (I_0) and transmitted X-ray (I), were filled with 50% Ar/N₂ mixture gas and 100 % Ar gas, respectively.

The EXAFS raw data were analyzed with UWXAFS analysis package,^[1] including background subtraction program AUTOBK,^[2] curve fitting program FEFFIT.^[3] The amplitude reducing factor S_0^2 for Ag was fixed at 0.95. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code.^[4] ATOMS^[5] was used to obtain the FEFF input code for crystalline materials.

7. Inductively coupled Atomic Absorption Spectroscopy (ICP-AES). Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer; model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA).

Oxidation of alkenes

Liquid phase oxidation of alkenes was carried out in a double neck round bottom flask in an oil bath connected with a spiral condenser (length 60 cm) using 0.10 g catalyst, 10 ml acetonitrile solvent and 1 g of substrate to which 50 % aqueous solution of H₂O₂ was added dropwise maintaining a substrate: H₂O₂ mole ratio 1:3. The condenser was attached to a

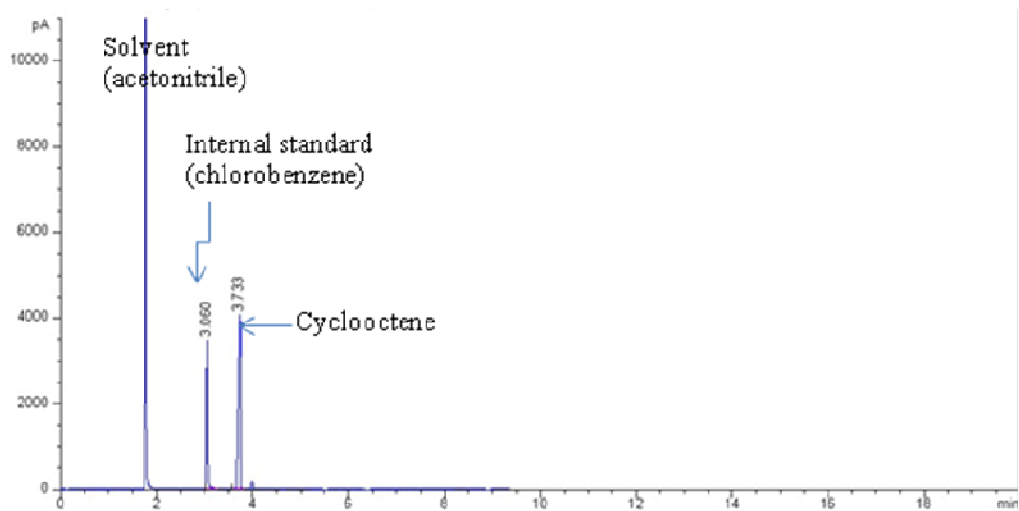
water circulating bath (Julabo, FC 600) maintaining a constant temperature of 10° C. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis. In case of propylene, the catalytic reaction was performed in a 100 ml high pressure teflon lined stainless steel closed reactor. Typically, 10 ml acetonitrile solvent along with 0.1 g catalyst were taken in the reactor and required amount of H₂O₂ was added. The closed reactor was pressurized with 10 bar propylene and the reactor was heated to the reaction temperature (80° C) with constant stirring by an external magnetic stirrer. The reaction was carried out for 16 h.

At the end of the reaction, the solid particles (catalyst) were separated by filtering during the hot condition and products were analysed by gas chromatograph (GC, Agilent 7890) connected with a HP-5 capillary column (30 m length, 0.28 mm id and 0.25 µm film thickness) and a flame ionization detector (FID). Conversion of substrate was calculated based upon the GC-FID results, where conversion = [moles of substrate reacted]/[initial moles of substrate used] x 100 and selectivity of products calculated by [total moles of product formed]/[total moles of substrate converted] x 100. The individual yields were calculated and normalized with respect to the GC response factors taking chlorobenzene as an internal standard. The GC response factor was determined changing the amount of cyclooctene (reactant) consequently, whilst keeping the amount of internal standard (chlorobenzene) fixed.

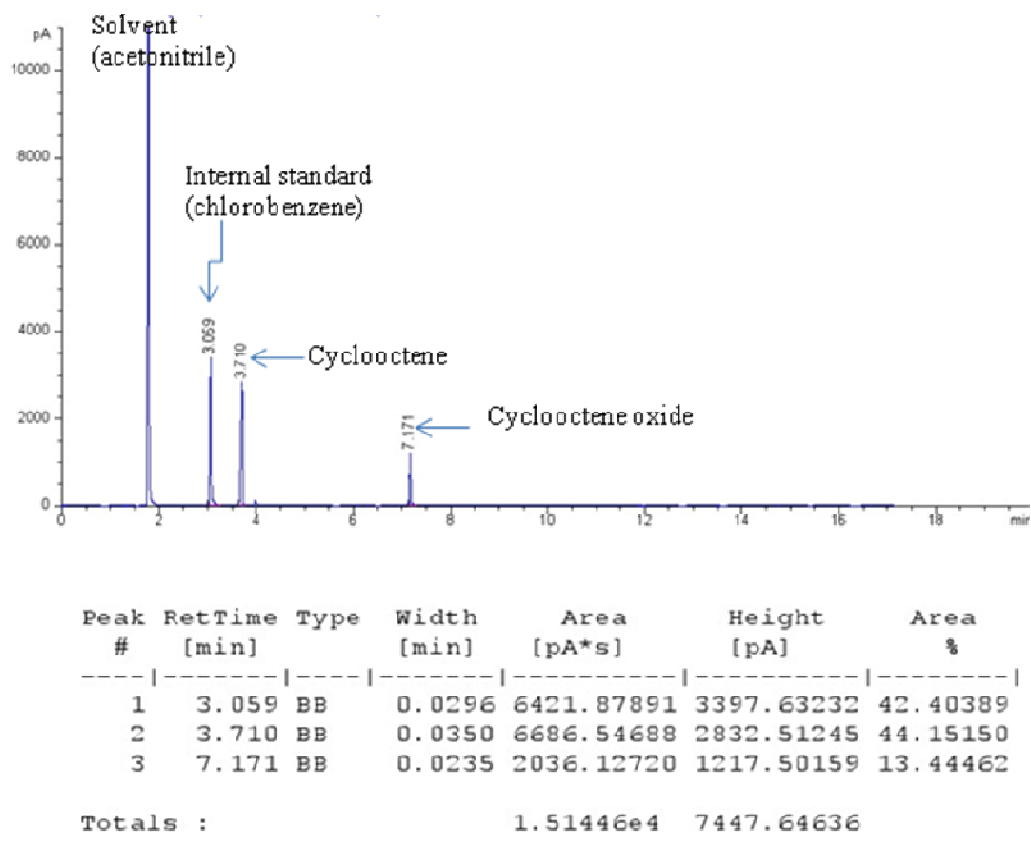
The product identification was carried out by injecting authentic standard samples in GC and GCMS and ¹H-NMR was taken to identify the product. The C- balance as well as material balance was carried out for most of the experiments and it was found between 98-102%. For the reusability test, after completion of the reaction, the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with acetone and reused as such for multiple circles.

Response factor calculation and material balance:

10 ml acetonitrile+ 0.75 g chlorobenzene (internal standard) + 1 g cyclooctene



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.060	BB	0.0285	6430.70166	3482.72900	35.82083
2	3.733	BB	0.0385	1.15217e4	4069.24780	64.17917
Totals :				1.79524e4	7551.97681	

After 1.30 h reaction,

Since amount of internal standard was fixed all time (0.75 g),

So, response factor = $6430.70/6421.87 = 1.001$

So, new area of cyclooctene = $6686.54 \times 1.001 = 6693.22$

Everytime we have injected 0.4 μ l. amount of sample.

Since, we have prepared solution containing 10 ml acetonitrile + 0.75 g internal standard =
0.67 ml internal standard + 1 g cyclooctene = 1.18 ml cyclooctene

Hence, total volume of solution prepared = 11.85 ml

So, 11.85 ml solution contains 1 g cyclooctene = $1/110$ mole

Hence, 0.4 μ l. solution contains = 0.306 micromole cyclooctene.

So, initial amount of cyclooctene = 0.306 micro mole whose area = 1.152×10^4

After 1.3 h reaction, 0.4 μ l. injected volume contains cyclooctene area= 6693.22 (after being normalised by response factor),

So, after 1.3 h reaction, amount of cyclooctene= 0.1293 micro mole

From here,

$$\begin{aligned}\text{conversion} &= [\text{moles of cyclooctene reacted}]/[\text{initial moles of cyclooctene used}] \times 100 \\ &= [0.3 - 0.1293]/0.3 = 56.9\end{aligned}$$

Hence, conversion of cyclooctene = ~57%

Carbon balance and material balance:

Initially,

0.3 μ mole cyclooctene = (0.3×8) micro mole Carbon= 2.4 μ mole carbon

and (0.3×14) μ mole H= 4.2 μ mole Hydrogen.

After reaction,

0.1293 μ mole cyclooctene = (0.1293×8) μ mole Carbon= 1.0344 μ mole carbon

and (0.1293×14) μ mole H= 1.8102 μ mole Hydrogen.

So, material balance was carried out by the following procedure,

2.4 μ mole carbon = 1.0344 μ mole carbon (cyclooctene) + x μ mole carbon (from product cyclooctene oxide)

And

4.2 μ mole Hydrogen = 1.8102 μ mole Hydrogen (cyclooctene) + y μ mole carbon (from product cyclooctene oxide).

The calibration of the product cyclooctene oxide taking internal standard (chlorobenzene) was performed in a similar process and the value of x and y was determined and it was found between 98-102%.

The efficiency of H₂O₂ was calculated as per the following equation:

$$\text{H}_2\text{O}_2 \text{ efficiency (E}_o\text{)} = [\text{Moles of epoxide formed} / \text{total moles of H}_2\text{O}_2 \text{ added}] \times 100$$

We have calculated the efficiency according to the paper by Borah et al. *Angew. Chem. Int. Ed.* 2012, 51, 7756–7761.

We have taken 1 gm of reactant (cyclooctene) initially and 99% cyclooctene conversion with 97% cyclooctene oxide selectivity was achieved.

$$\text{So, moles of epoxide formed} = (99 \times 97) / (10^4 \times 110) = 9603 / (10^4 \times 110)$$

(since mol. wt. of cyclooctene is 110)

During the reaction cyclooctene : H₂O₂ mole ratio = 1:3

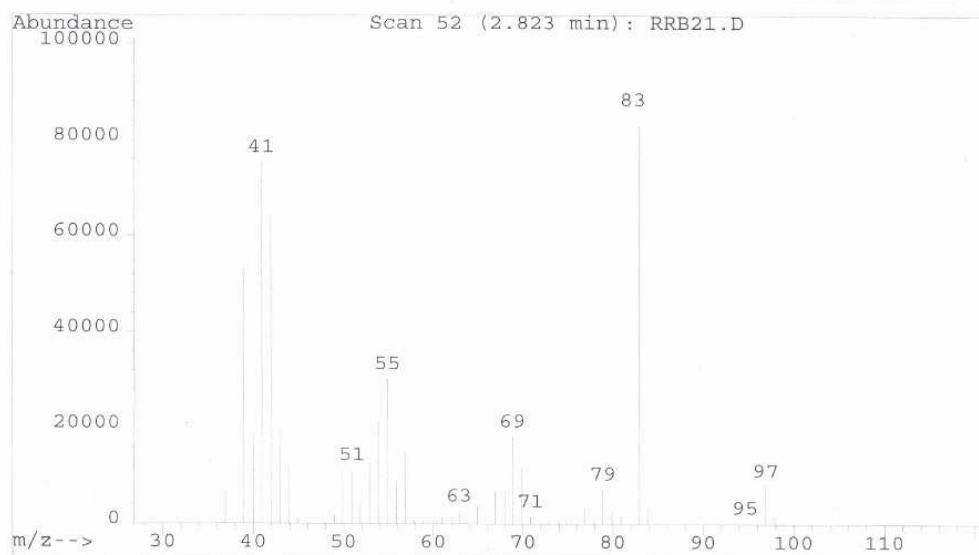
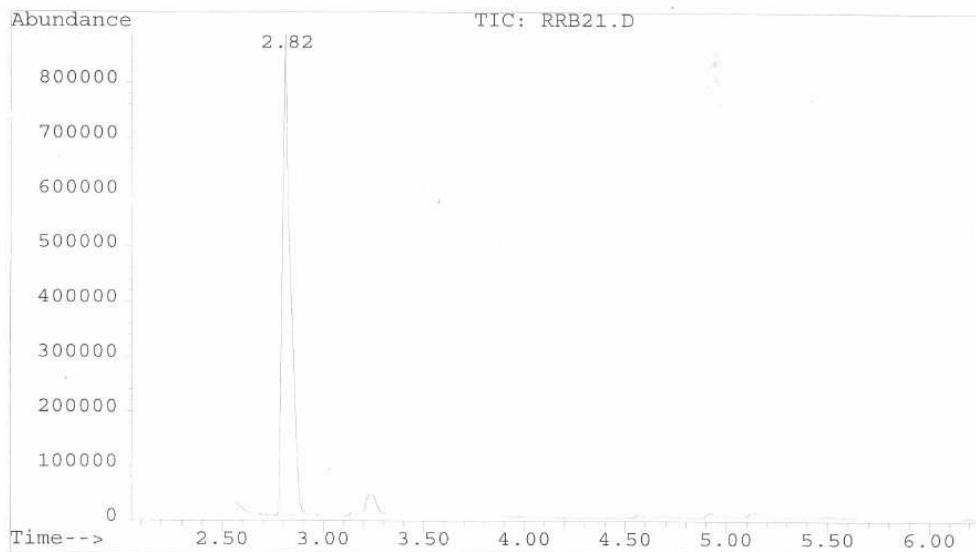
$$\text{So, total moles of H}_2\text{O}_2 \text{ added} = (1 \times 3 \times 34) / (110 \times 34) = 3/110$$

(since mol. wt. of H₂O₂ is 34)

$$\text{Hence, E}_o \text{ (H}_2\text{O}_2 \text{ efficiency)} = [\text{Moles of epoxide formed} / \text{total moles of H}_2\text{O}_2 \text{ added}] \times 100$$

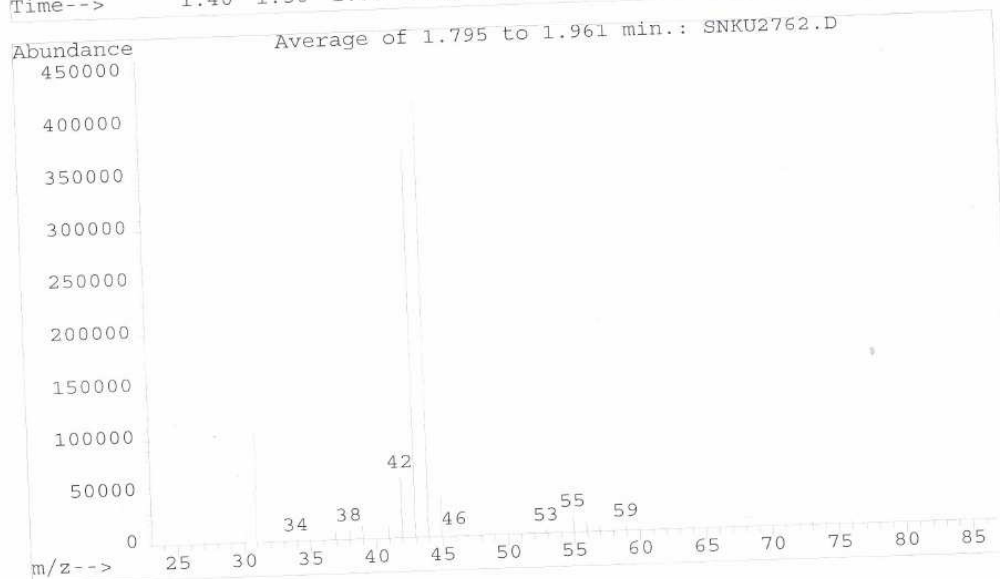
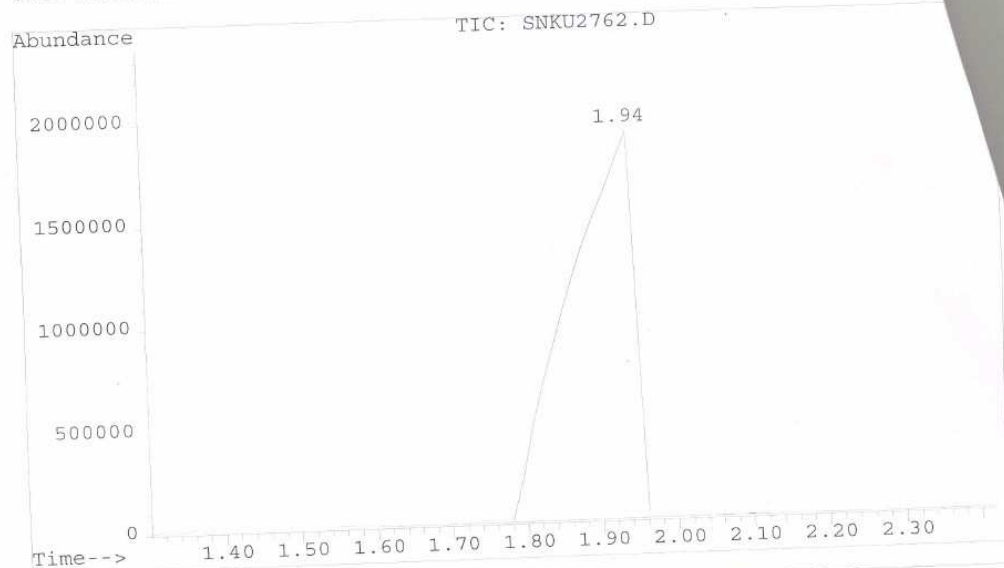
$$= (9603 / 10^4 \times 110) \times (110 / 3) = 32.0 \text{ (Table 3, entry 6 in the main manuscript)}$$

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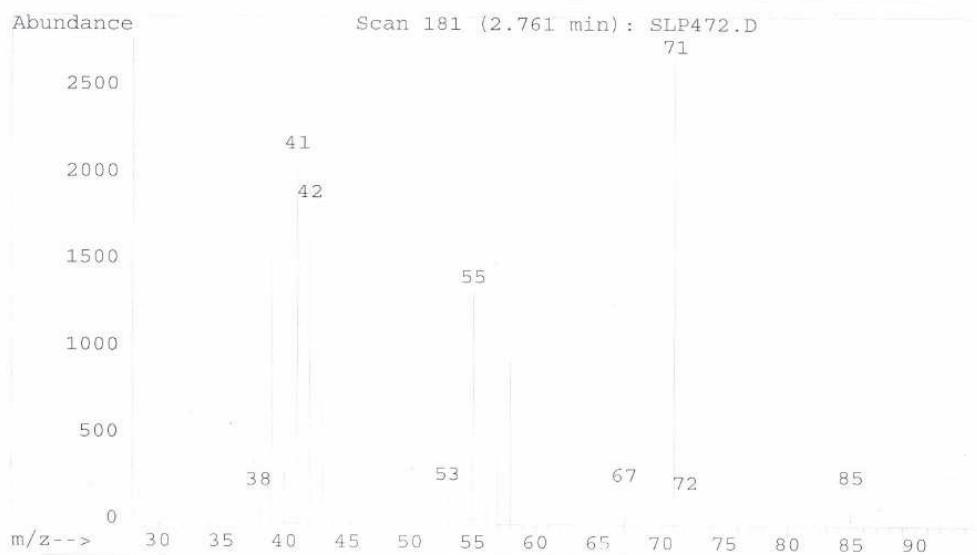
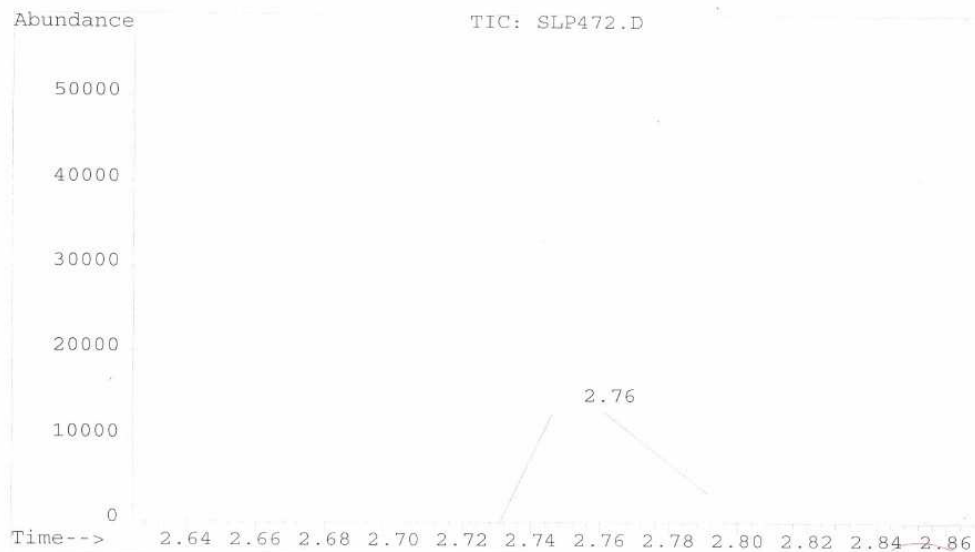
GC-MS OF CYCLOHEXENE OXIDE

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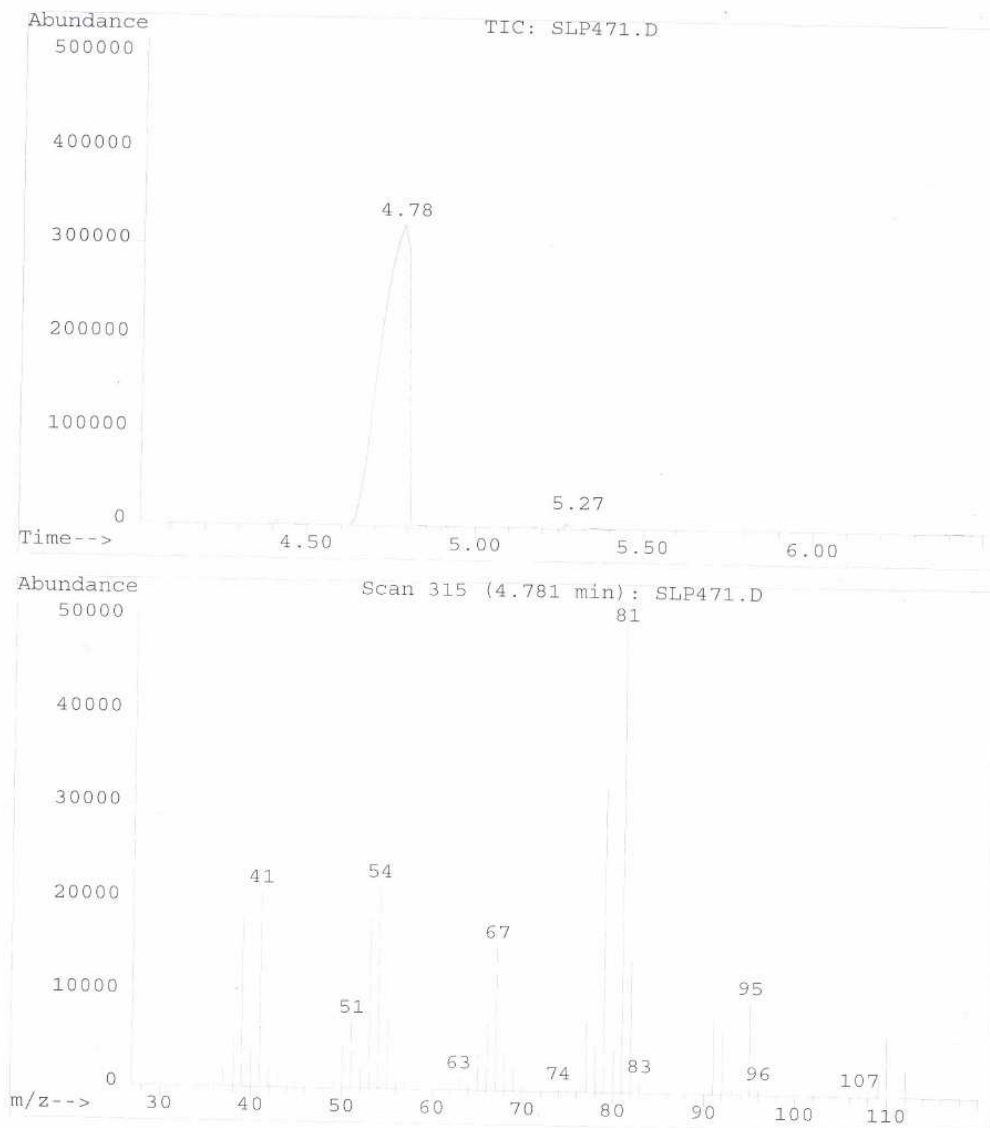
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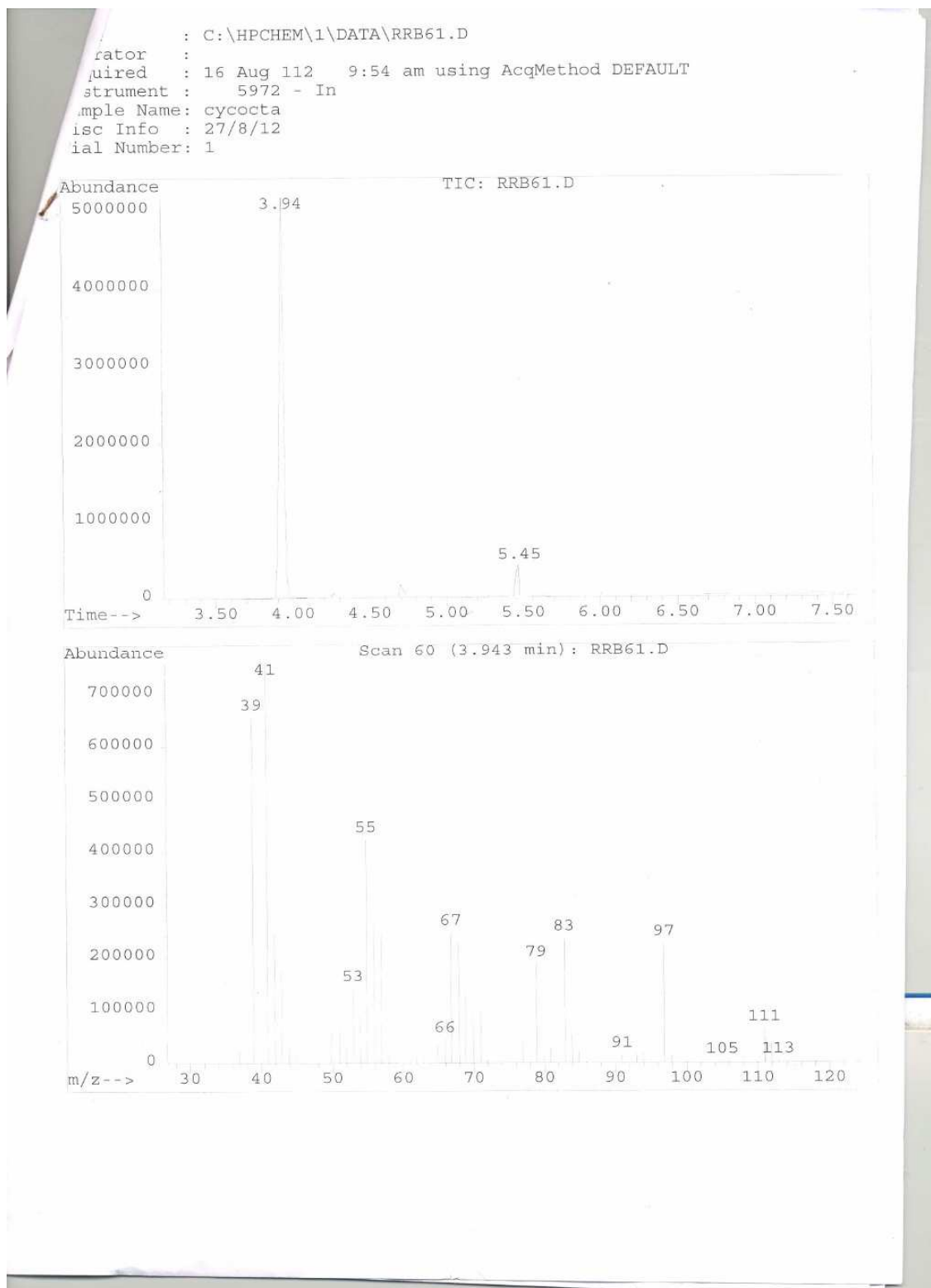


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GC-MS OF NORBORNENE OXIDE



GC-MS OF CYCLOHEPTENE OXIDE

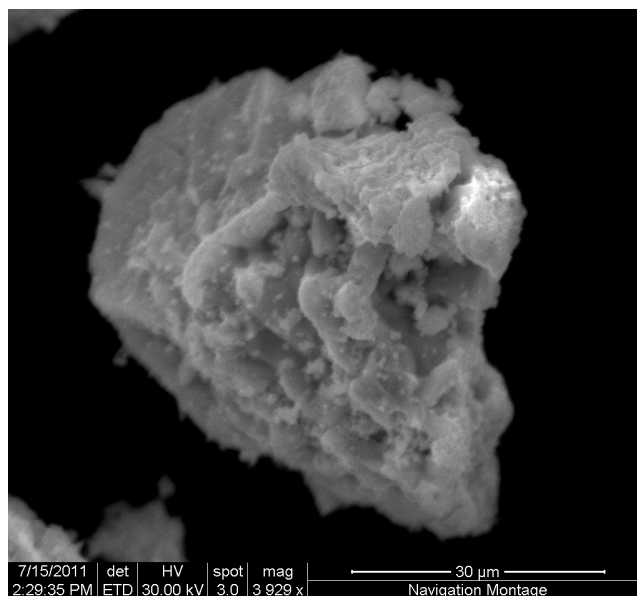


Fig. S1 SEM image without addition of CTAB.

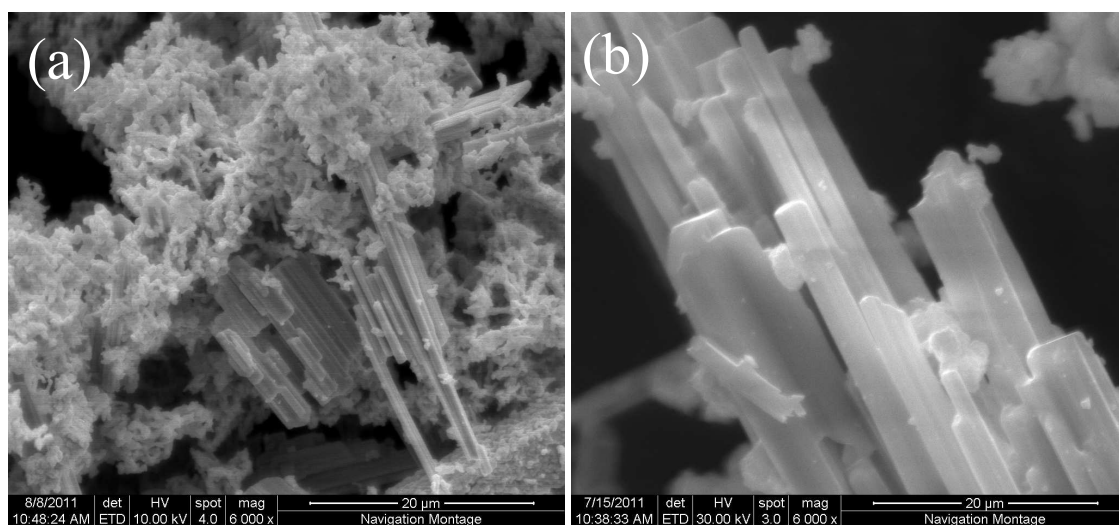


Fig. S2 SEM image a) 30 min stirring before hydrothermal process, b) 1 h stirring just before hydrothermal process.

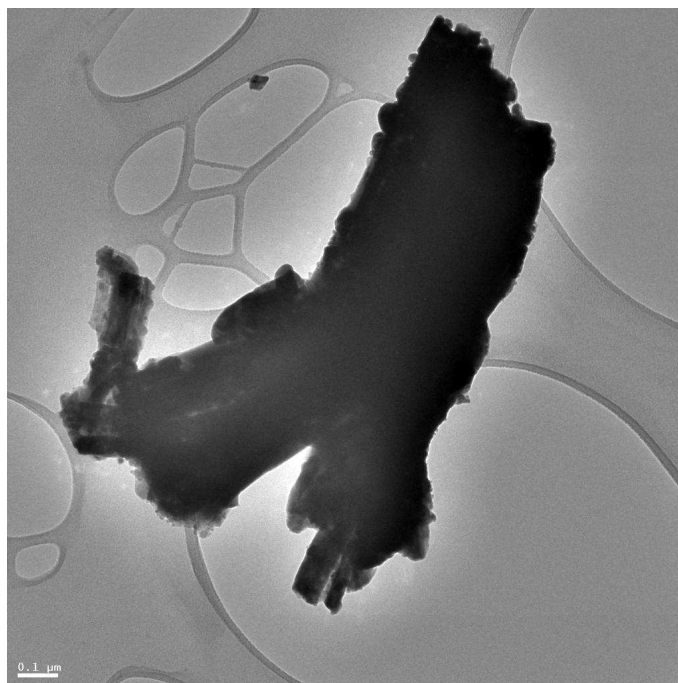


Fig. S3 TEM image after 1 hr HT process.

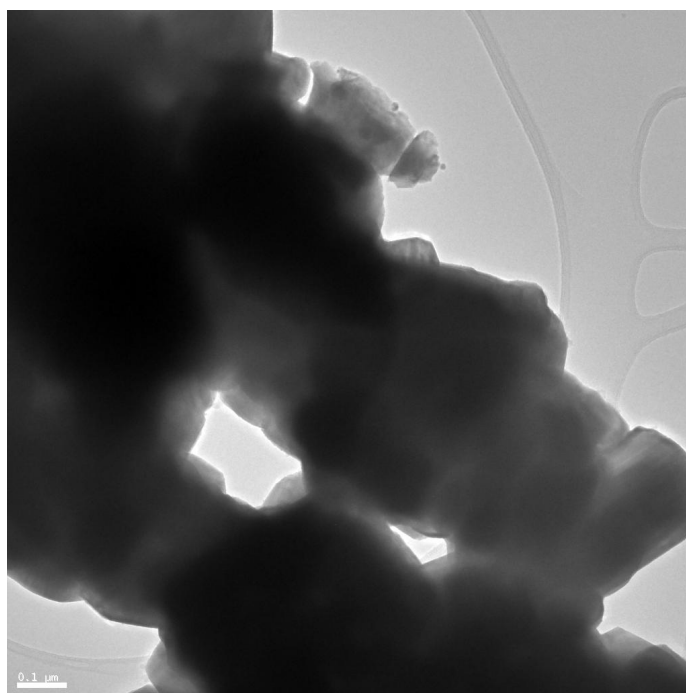


Fig. S4 TEM image after 24 hr HT process.

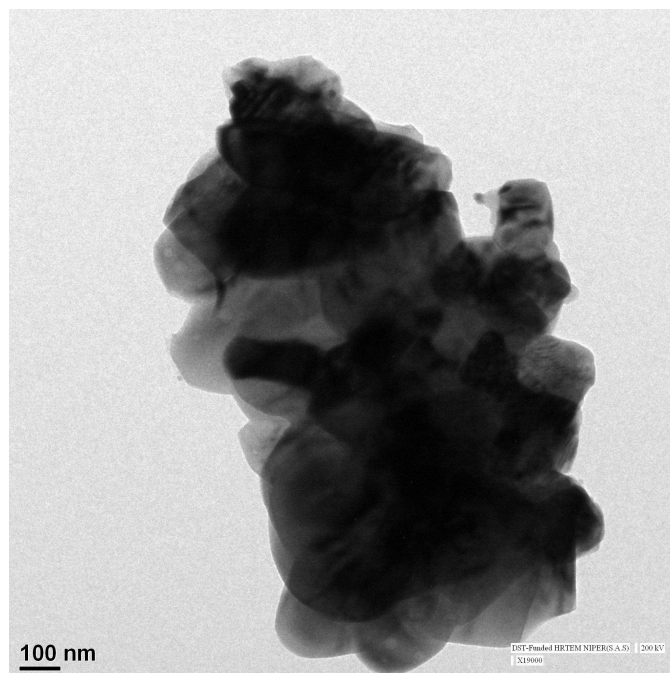


Fig. S5 TEM image after Ag:CTAB=1:0.15.

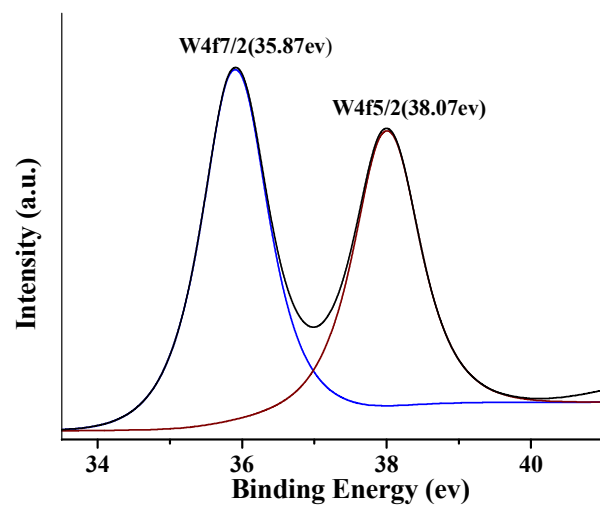


Fig. S6. W4f_{7/2}, W4f_{5/2} core level spectra of the fresh Ag/ WO₃ catalyst.

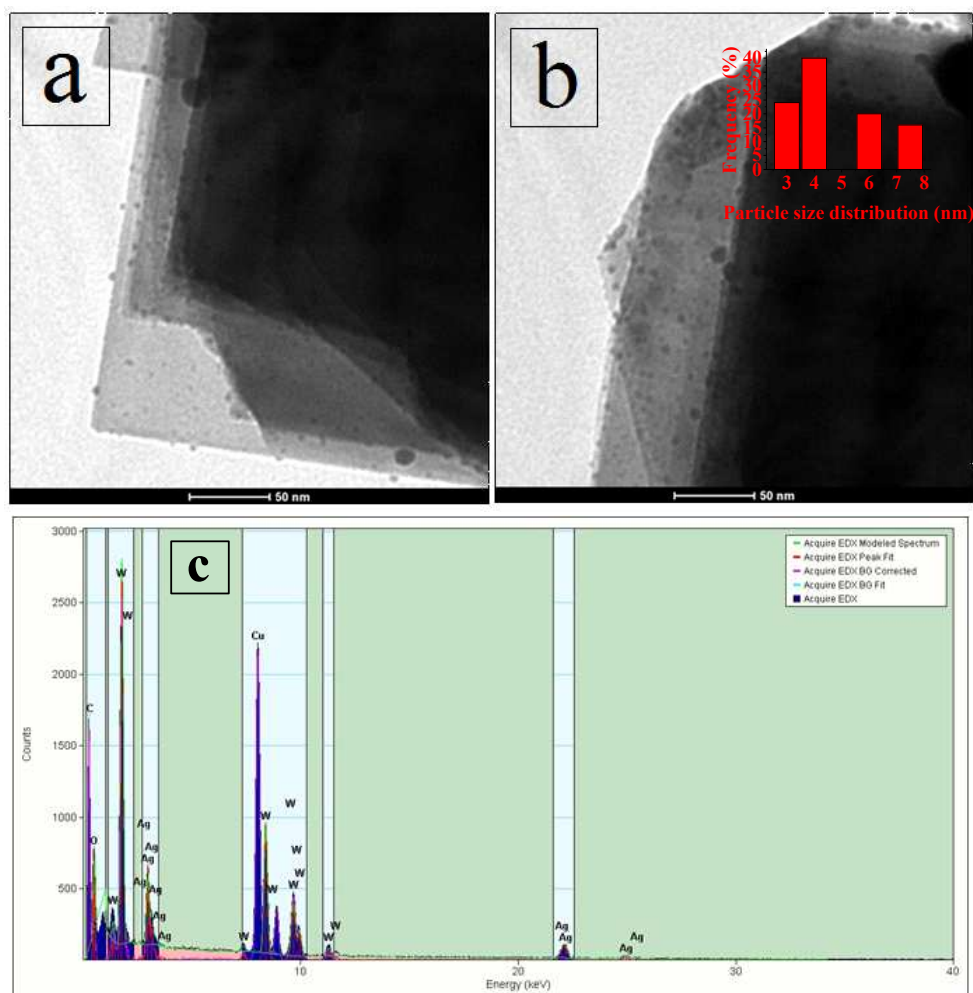


Fig. S7. TEM image of a) fresh Ag/WO₃ nanolayered catalyst, b) spent catalyst (inset, silver particle size distribution) and c) TEM EDX.

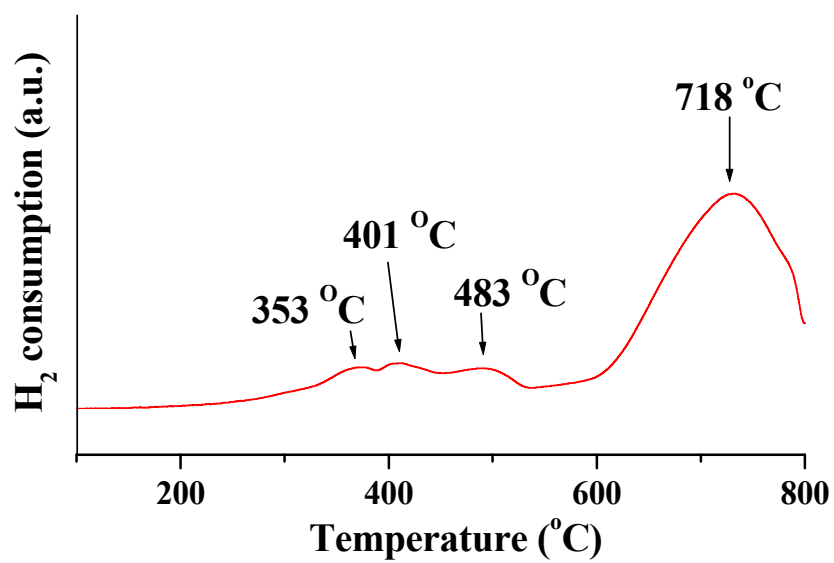


Fig. S8. TPR of Ag/WO₃ catalyst

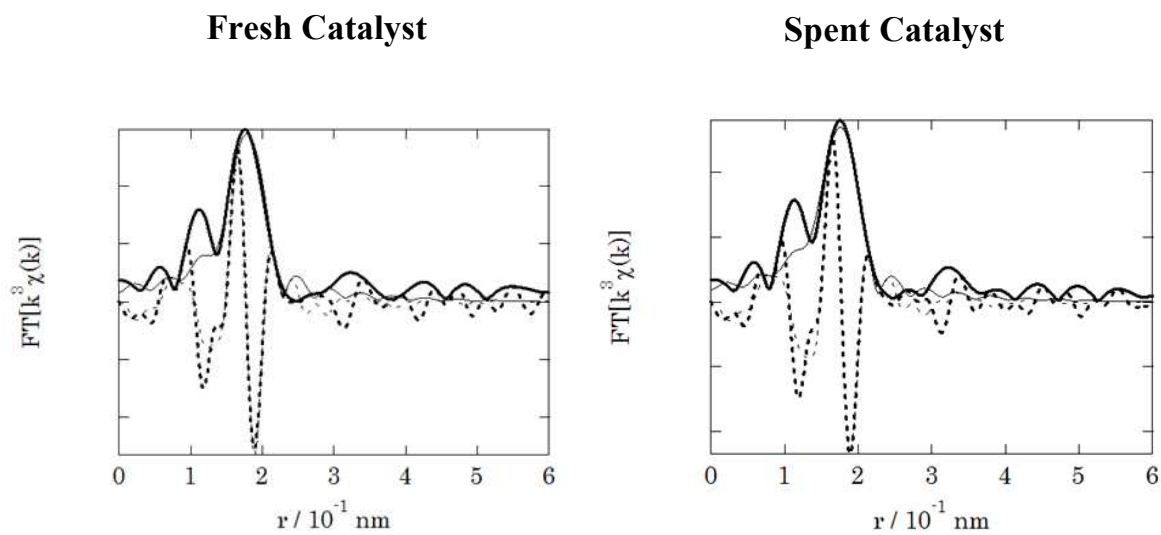


Fig. S9. EXAFS spectra of fresh Ag/ WO_3 catalyst, and spent catalyst. Amplitude: solid curves; imaginary part: dotted curves; observed data: thick curves; fitting data: thin curves.

Table S1. Catalytic activities of different reported catalysts for alkene epoxidation reaction.

Catalyst	Substrate	Solvent	H ₂ O ₂ (wt %)	Mole ratio Substrate: H ₂ O ₂	Temp (°C)	Time (h)	Conv. (%)	Sel. (%)	Ref.
TS-1	1-Hexene	Acetonitrile	30	1:1	60	2	16.5	98	6
W-Zn/SnO ₂	Cyclooctene	DMC	60	1:1	60	4	99	99	7
Ga ₂ O ₃	Cyclooctene	Ethyl acetate	50	1:2	80	4	84	99	8
Ga ₂ O ₃	Styrene	Ethyl acetate	50	1:2	80	4	20	58	8
MoO ₃ /SiO ₂	Cyclooctene	Decane	TBHP as oxidant	1:1	80	2	90	100	9
Ag ₂ O/WO ₃	Cyclooctene	Acetonitrile	50	1:3	80	3	99	97	This work
Ag ₂ O/WO ₃	Styrene	Acetonitrile	50	1:3	80	12	58	61	This work
Ag ₂ O/WO ₃	1-Hexene	Acetonitrile	50	1:3	RT	18	55	99	This work

Table S2. Comparative study of catalytic activities of previously reported catalyst and the catalyst prepared in this current work for alkene epoxidation reaction.

Catalyst	Silver particle size (nm)	Substrate	Mole ratio Substrate: H ₂ O ₂	Temp (°C)	Time (h)	Conv. (%)	Selectivity (%)	Catalyst reusability	Ref.
Ag/WO ₃ Previous work	10-70	Cyclooctene	1:3	80	3	43	51 (cyclooctene oxide selectivity)	Agglomerated particles after reaction at this reaction condition	Previous work (Journal of Advanced catalysis Science and Technology) ref. 10
Ag ₂ O/WO ₃ This work	3-8	Cyclooctene	1:3	80	3	99	97 (cyclooctene oxide selectivity)	Catalyst stable upto 5 runs at this reaction condition, particle size and morphology remained same	This work
Ag/WO ₃ Previous work	10-70	Propylene (10 bar propylene pressure)	1:3	80	16	7	47 (propylene oxide selectivity) selectivity less due production of acrolein, acetic acid as the major side product	Agglomerated particles after reaction at this reaction condition and rapid deactivation of the catalyst	Previous work (Journal of Advanced catalysis Science and Technology) ref. 10
Ag ₂ O/WO ₃ This work	3-8	Propylene (10 bar propylene pressure)	1:3	80	16	42	99 (propylene oxide selectivity)	Catalyst stable upto 5 runs at this reaction condition, particle size and morphology remained same	This work

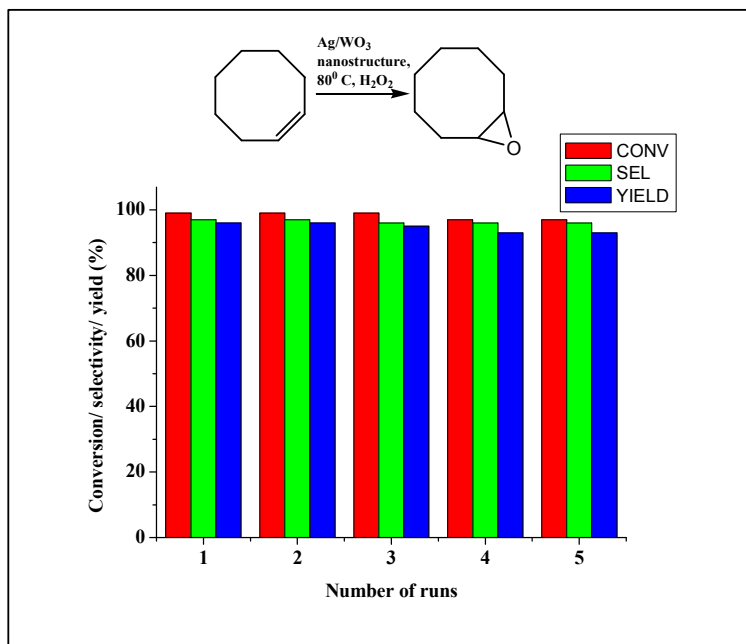
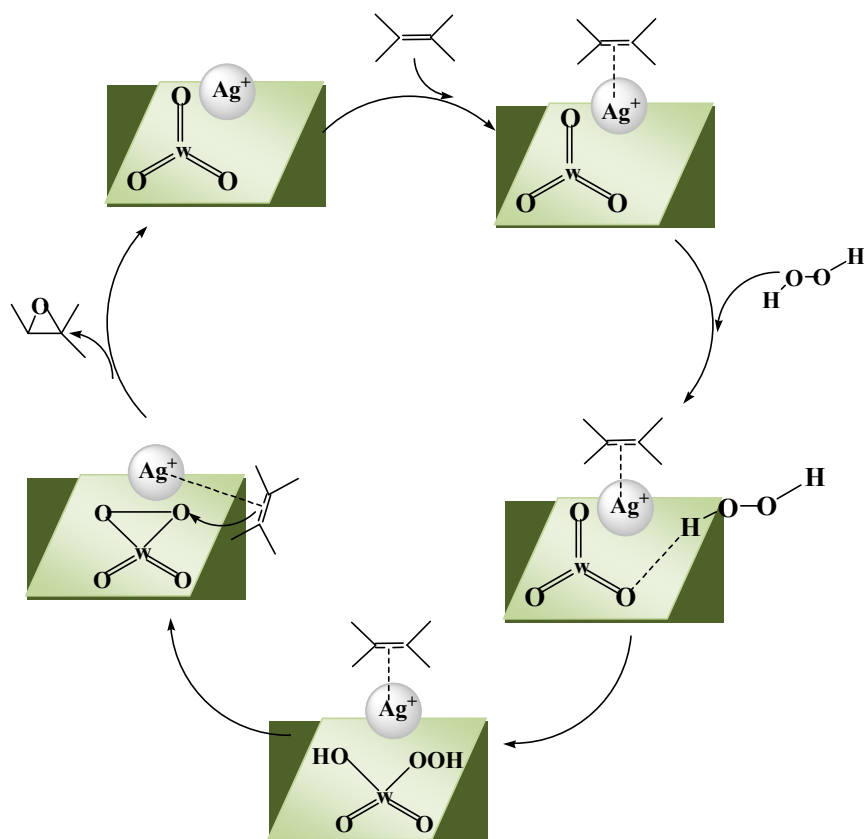


Fig. S10. Recyclability test of Ag/WO₃ nanocatalyst for the oxidation of cyclooctene to cyclooctene oxide.

Reaction Condition: solvent= acetonitrile; cyclooctene =1g; weight of catalyst = 0.10 g;
cyclooctene: H₂O₂ mole ratio =1:3; temperature = 80 °C, time= 3 h.



Scheme S1.Plausible mechanism for the formation of epoxide.

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