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Electronic Supplementary Information (ESI†)

One-pot preparation of nanocrystalline Ag/WO_3 catalyst for the selective oxidation of styrene

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Experimental Section

Materials and Methods

Hydrogen Peroxide (50 wt % in water) was purchased from Merck KGaA, Darmstadt, Germany. Tungstic acid, anhydrous silver nitrate, cetyltrimethylammonium bromide (CTAB), hydrazine (80% aq. solution), ammonium hydroxide, styrene (purity > 99.9%), acetonitrile (HPLC grade) were purchased from Sigma-Aldrich Co. All the chemicals were used without further purification.

Synthesis of Ag/WO_3 Aloevera Catalyst

In a typical preparation method, 10.8 g tungstic acid was dipersed in 17g water to give a yellow-coloured solution. Then, aqueous solution of 0.55 g silver nitrite was added dropwise. The pH of solutions was measured by pH Meter, which was standardized for pH measurement prior to use. By gradual addition of few drop ammonia solution, the pH of the solution was made 8; the colour of the solution became greyish gradually. Then aqueous solution of CTAB (3.6 g) was added in the mixture, followed by intensive stirring for 2h. A solution of hydrazine (0.45 g) monohydrate (80% aqueous solution) was added drop wise to the well stirred mixture at RT by simultaneous, vigorous agitation. All the reagents were used maintaining the ratio: Ag: CTAB: hydrazine: H_2O = 1: 3: 1.5: 300. The mixture was stirred vigorously for 30 min. After 30 min stirring, the mixture was aged at 40 °C for 3 h. After that, it was agitated thoroughly by ethanol. Thick white precipitation occurred. After that, these white fluffy solid products (precipitates) were collected by centrifugation at 7500 rpm and washed with water and ethanol several times prior to drying in air at 100 °C for 6h. The resulting dry powder was transferred to a quartz reactor inside a tubular resistance furnace for calcination. After calcinations, the so obtained canary-yellow powder was collected for characterization and reactions.

Characterization Techniques

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 using Cu Ka radiation with a wavelength of 1.5418 Å. Diffraction patterns in the 2°-80°region were recorded at a rate of 0.5 degrees (2θ) per minute. The resulting XRD profiles were analyzed to identify the crystal phase of the compound using reference standards. The line width of the most intense XRD peak was taken for estimation of crystallite size by the Scherrer equation. Scanning electron microscopy (SEM): Scanning electron microscopy images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (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. Samples were subjected to scanning electron microscope analysis to understand the shape, size, and morphology properties. Transmission electron microscopy (TEM): The particle size and distribution of the samples were analyzed by TEM, JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. 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. The resulting spectra were analyzed to identify the different oxidation states of the copper and chromium ions present in the sample. Prior to the analysis, the spectra were calibrated with reference to C1s observed at a binding energy of 284.5 eV. 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). Thermogravimetric Analyses (TGA) of the uncalcined catalyst were carried out in a Pyris Diamond, Perkin Elmer Instruments and Technology by SII (Seiko Instruments INC), USA] instrument-balance by heating 2.15 mg samples at 5 °C min^{-1} in flowing air atmosphere. Raman spectra was measured at 298K by using a Laser Raman Spectrometer (JASCO, NRS-3100) with the 532 nm line from a diode-pumped solid-state laser for excitation. Fourier transform infra-red (FT-IR) spectra were recorded on a Thermo Nicolet 8700 (USA) instrument with the operating conditions: resolution: 4 cm^{-1}, scan: 36, operating temperature: 23–25 °C and the frequency range: 4000-400 cm^{-1}. Spectra in the lattice vibrations range were recorded for wafers of sample mixed with KBr.

Liquid Phase Catalytic Reaction

Liquid phase oxidation reaction was carried out in a two neck round bottom flask, equipped with refrigerant, containing 0.1 g catalyst, 10 ml solvent and 1 g styrene to which H_2O_2 (50% aq. solution) was added dropwise to prevent immediate H_2O_2 decomposition. The flask was then emerged in a preheated oil bath and vigorously stirred with a magnetic stirrer. The reaction temperature was ranged between RT and 90 °C. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. At the end of the reaction, the solid particles (catalyst) were separated by filtration and the products were analysed by Gas Chromatograph (GC, Agilent 7890) connected with a HP5 capillary column (30m length, 0.28 mm id, 0.25 µm film thickness) and flame ionisation detector (FID). Chem Station software was used to collect and analyze the respective GC-data. The styrene conversion and product selectivity were calculated using a calibration curve (obtained by manual injecting the authentic standard compounds). An anisole solution with a known amount was used as an external standard for analysis. The individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting the authentic standard samples in GC and GC-MS. For the reusability test, the catalyst was repeatedly washed with acetone and dried overnight at 110 °C and used as such, without regeneration. In order to check the metal leaching the mother liqor was then analyzed using ICP-AES. The C- balance as well as material balance was carried out for most of the experiments and it was found between 98-102%.

Material Balance.

We have performed the C-balance for the most of the experiments and have also done the material balance for few experiments. The estimated error in analysis arising due to sampling and handling losses was ± 5%. The C- balance as well as material balance was carried out for most of the experiments and it was found between 98-102%.

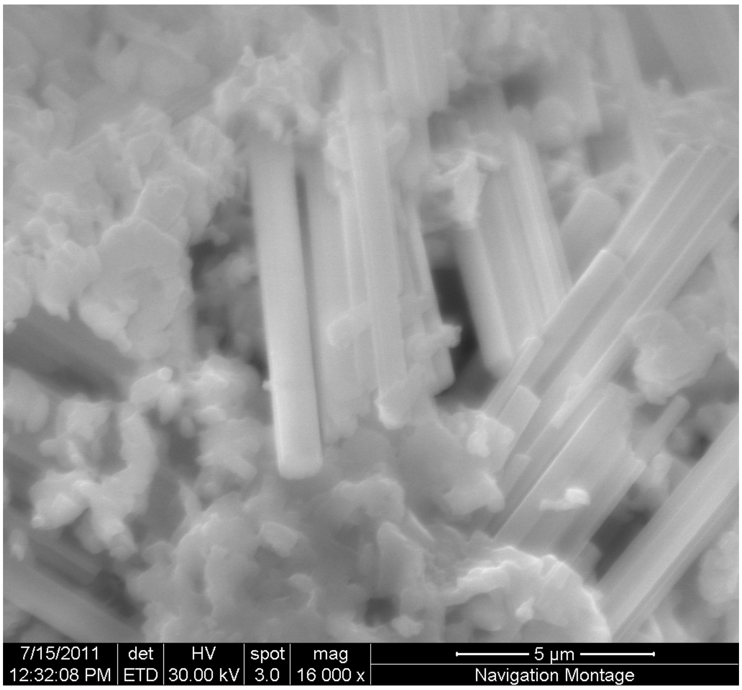

Figure S1. SEM image of the Ag/WO_3 catalyst without CTAB.

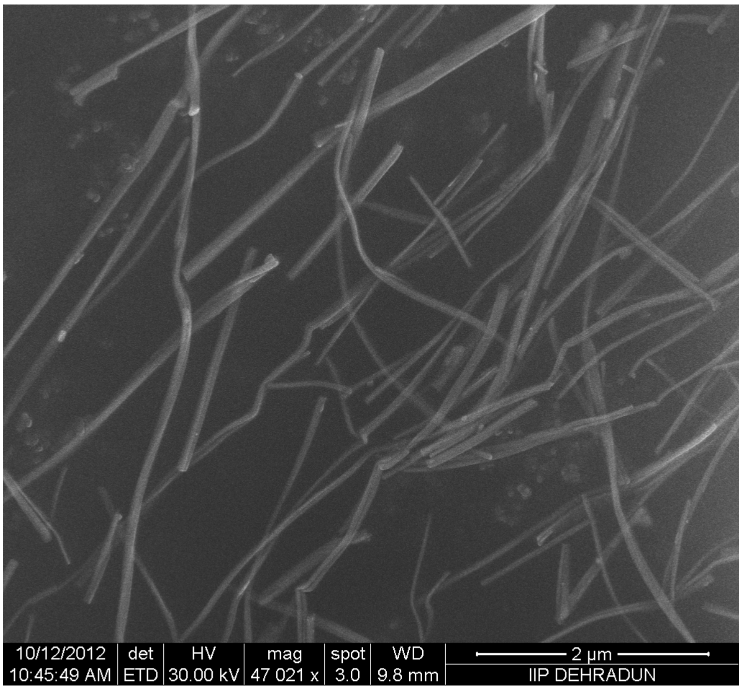

Figure S2. SEM image of the Ag/WO_3 catalyst when Ag: CTAB= 1:1.

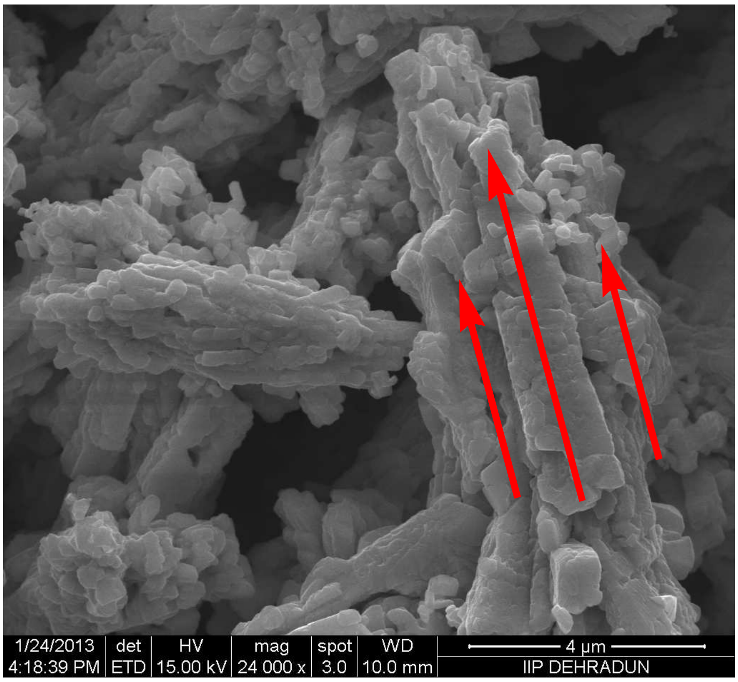

Figure S3. SEM image of the Ag/WO_3 catalyst when aging time was 1h.

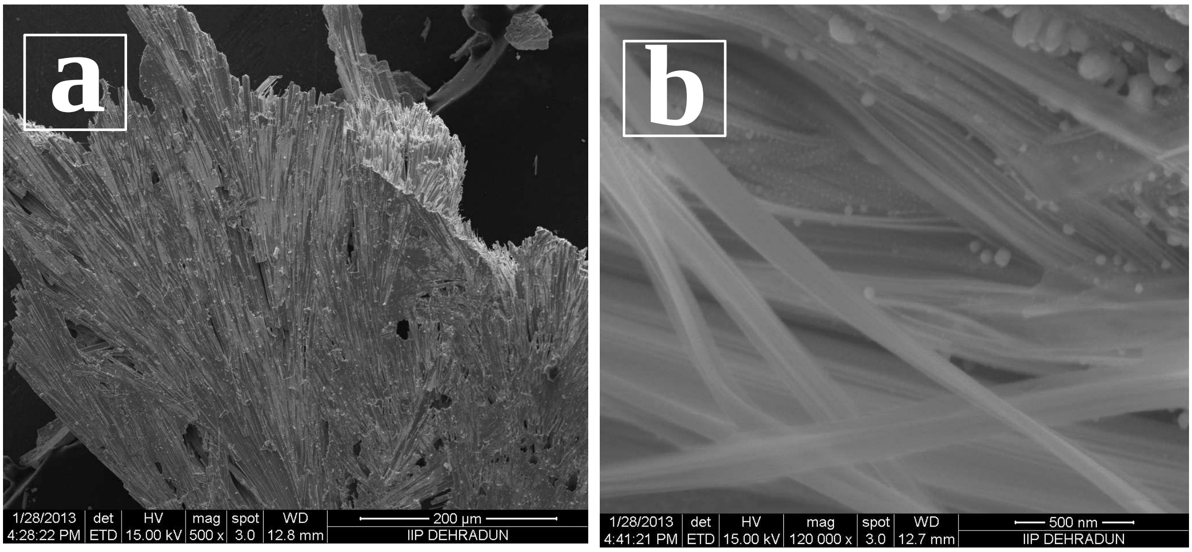

Figure S4. SEM image of the Ag/WO_3 catalyst when aging time was 3 h.

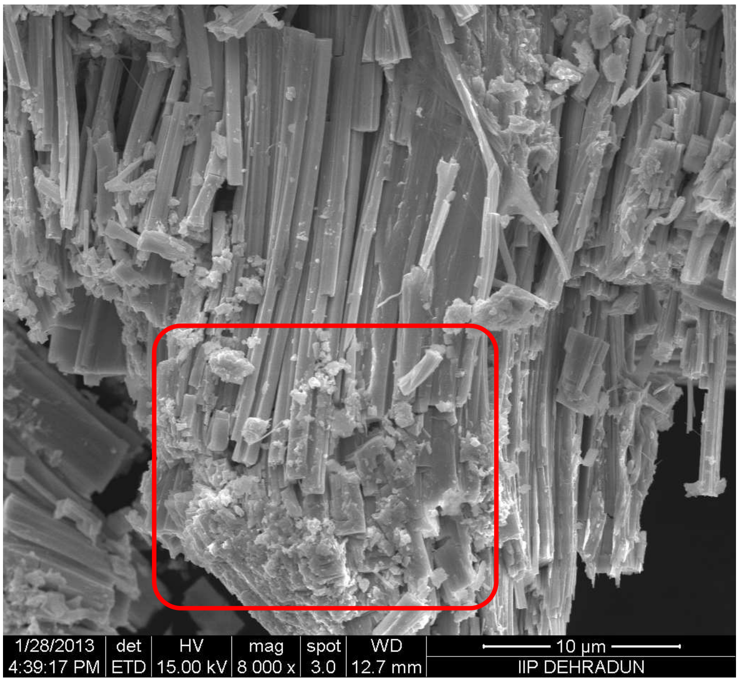

Figure S5. SEM image of the Ag/WO_3 catalyst when aging time was 10 h.

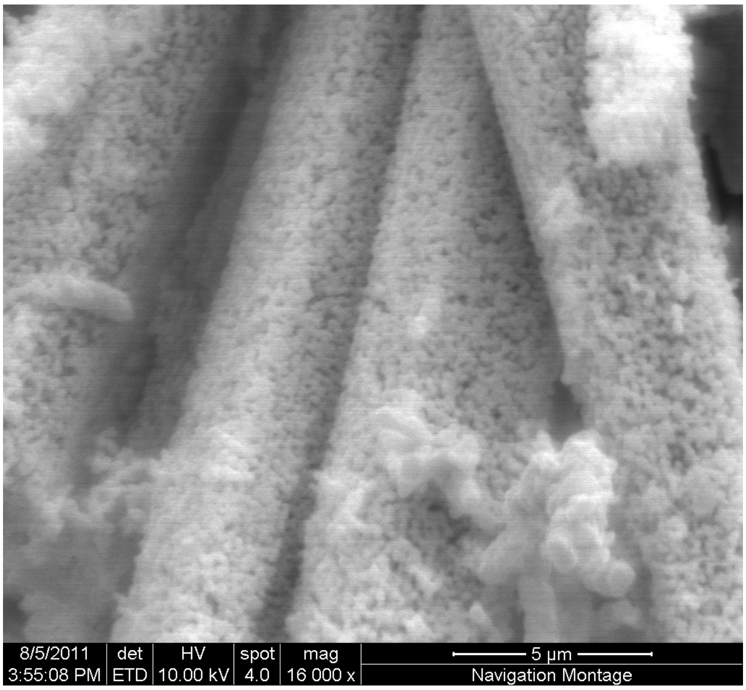

Figure S6. SEM image of the catalyst when $AgNO_3$ was not added.

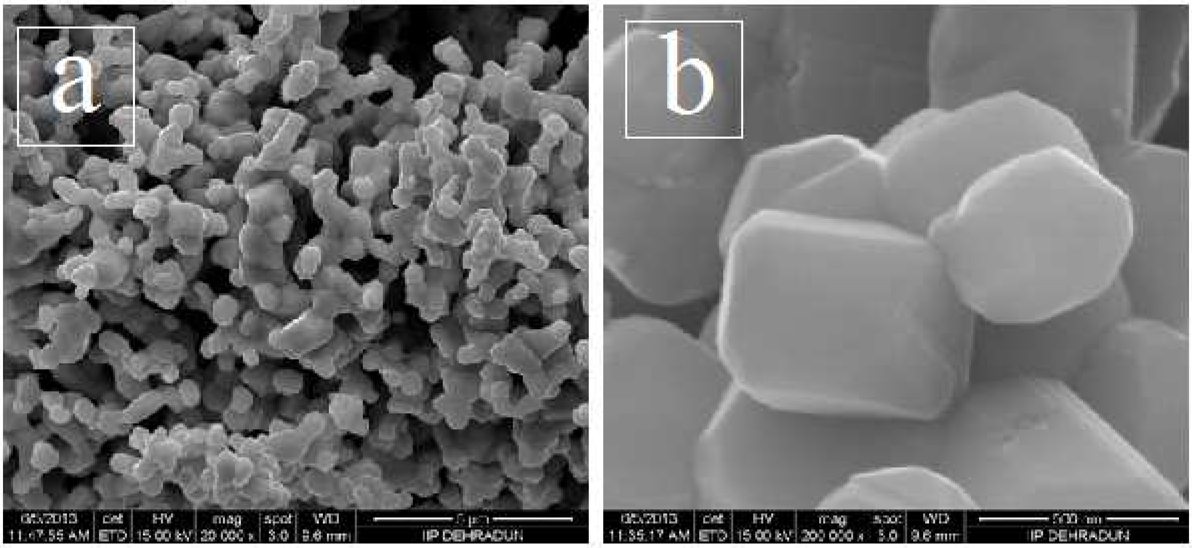

Figure S7. SEM images of the Ag-W nanocomposites taking chloride precursors of Ag & W.

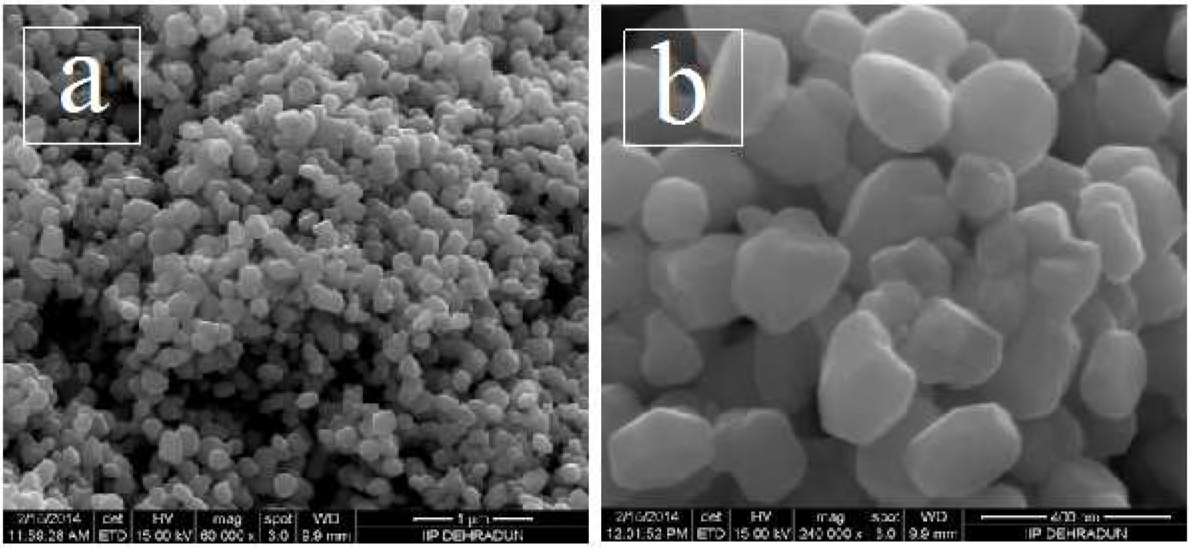

Figure S8. SEM images of the Ag-W nanocomposites taking nitrate precursors of Ag (i.e. $AgNO_3$) and ammonium metatungstate.

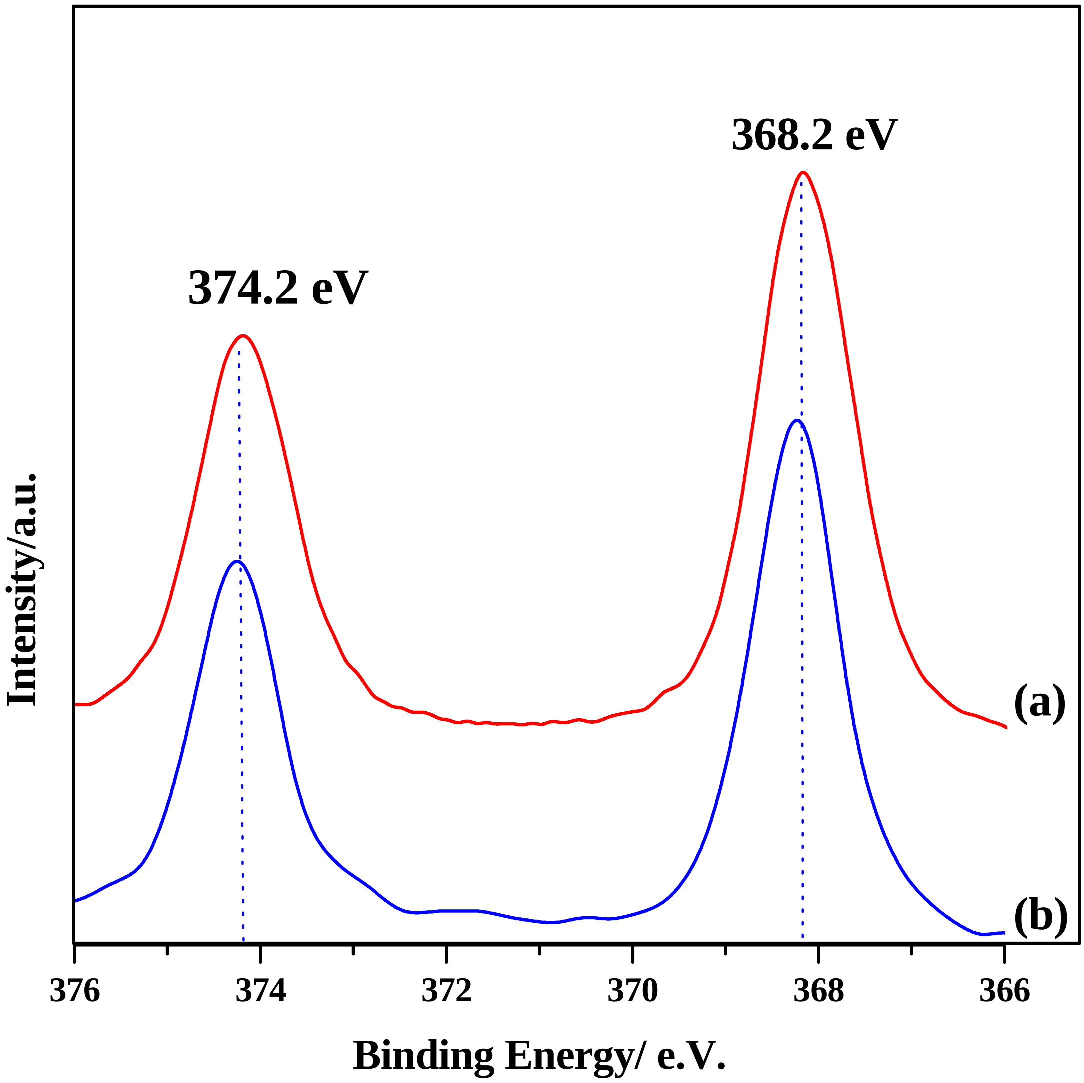

Figure S9. Ag3d-core level spectra (XPS) (a) fresh catalyst and b) spent catalyst.

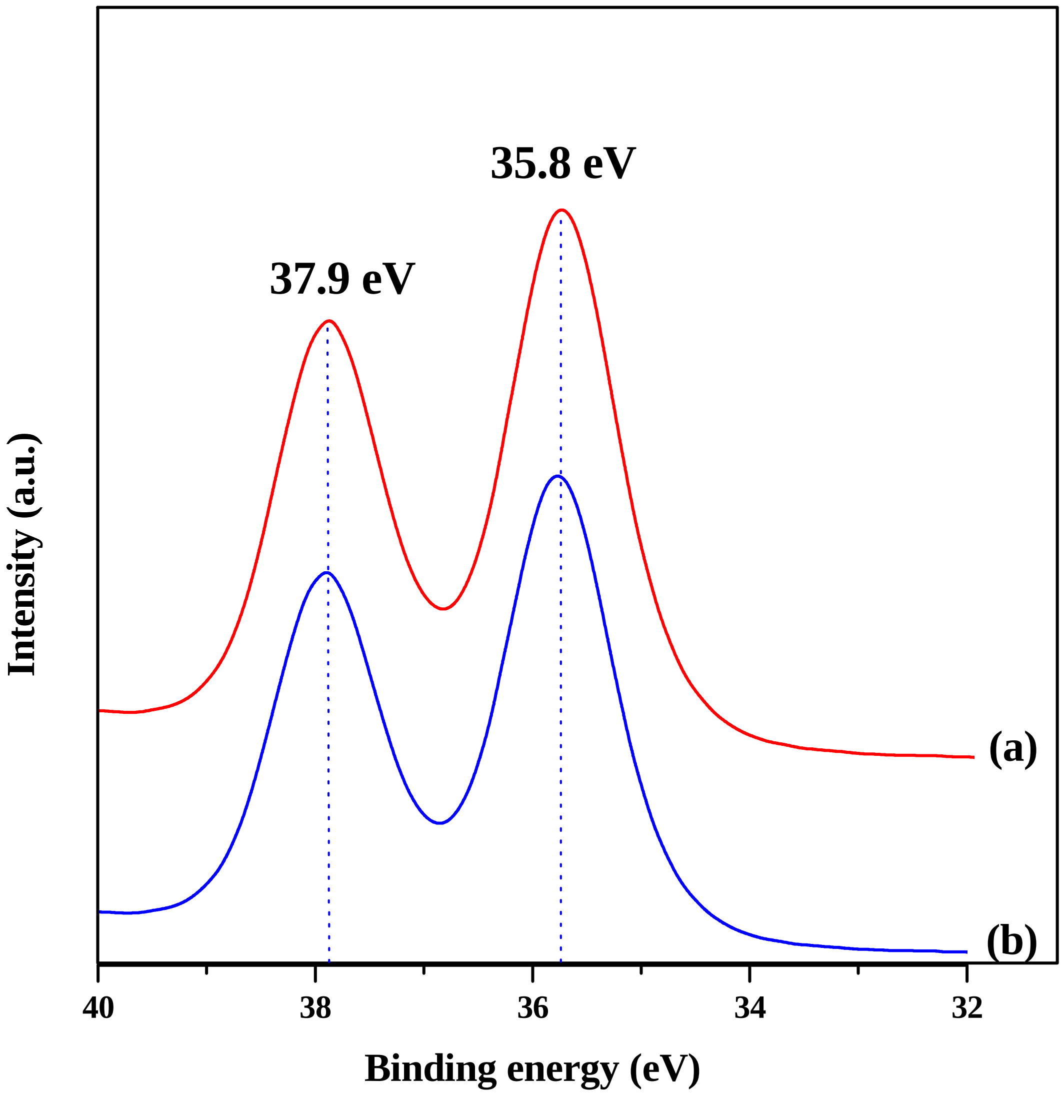

Figure S10. W4f-core level spectra (XPS) a) fresh catalyst and b) spent catalyst.

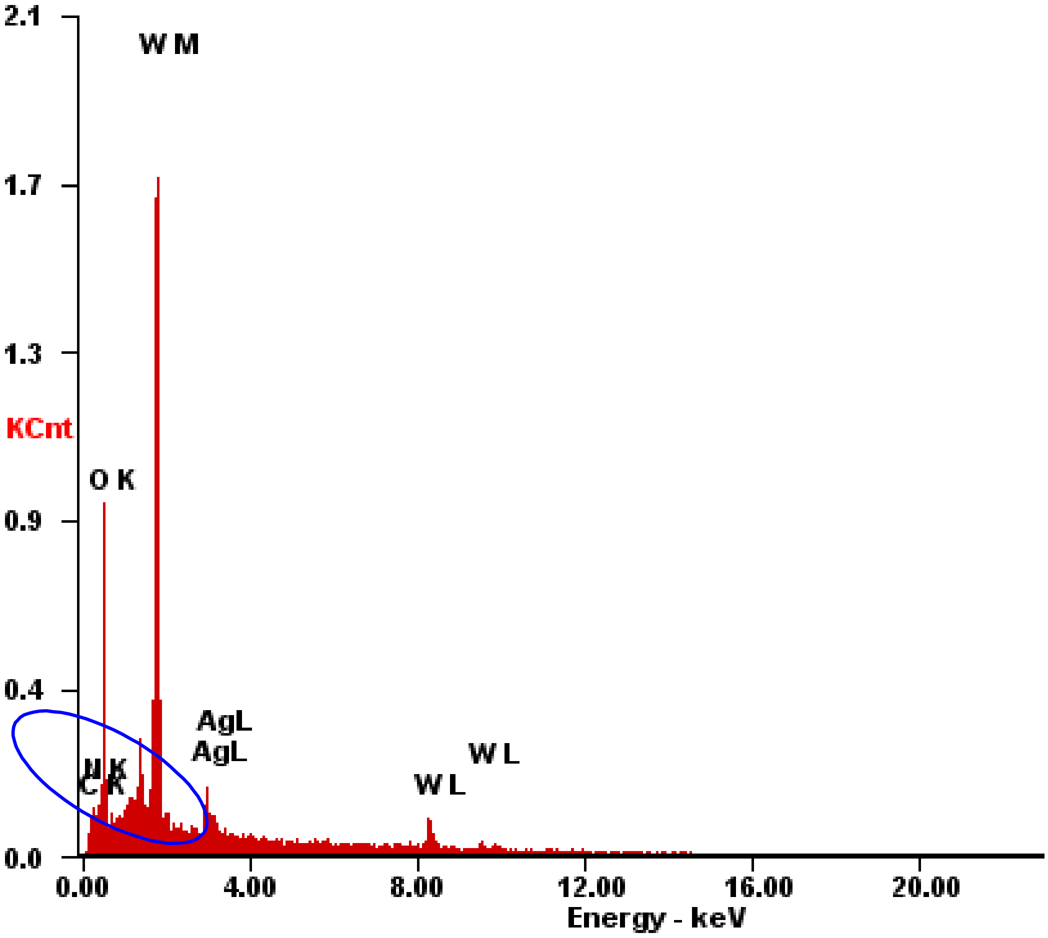

Figure S11. SEM-EDAX of the uncalcined Ag/WO_3 catalyst.

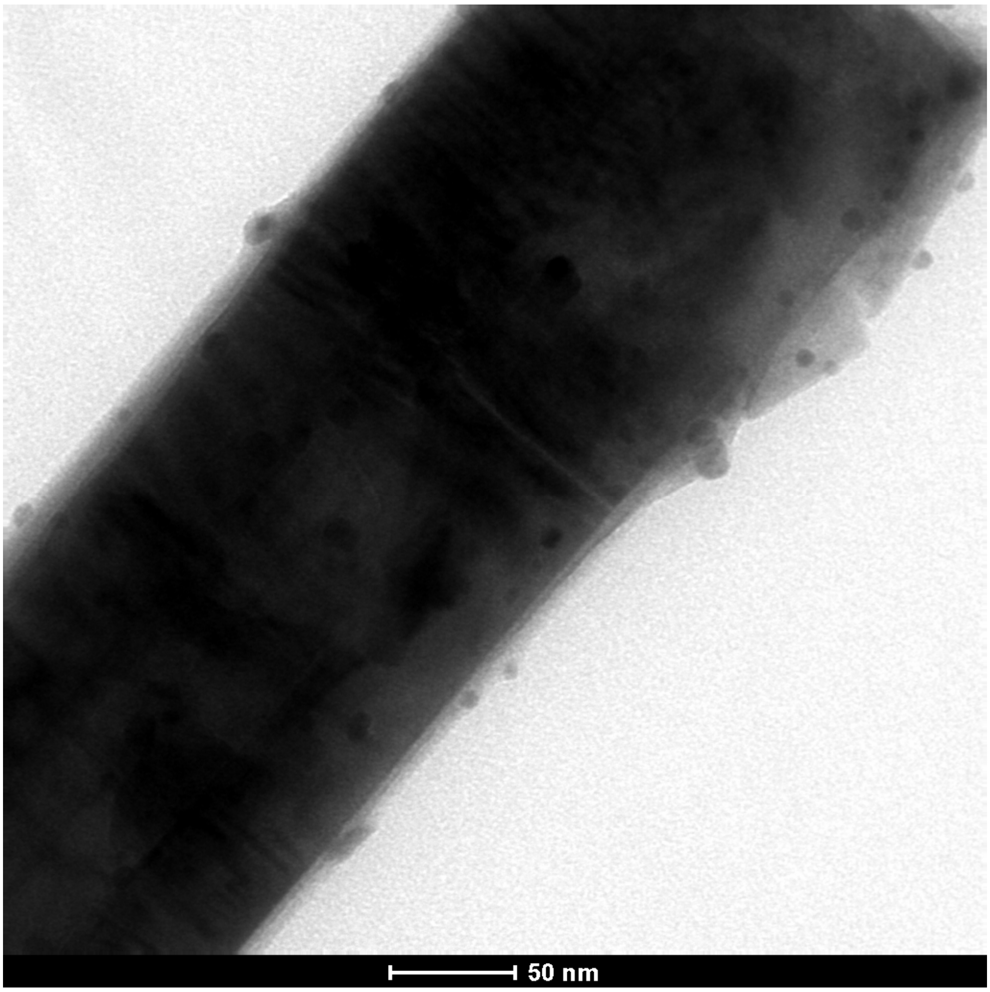

Figure S12. TEM diagram of the Ag-WO_3 spent catalyst (after 5reuses).

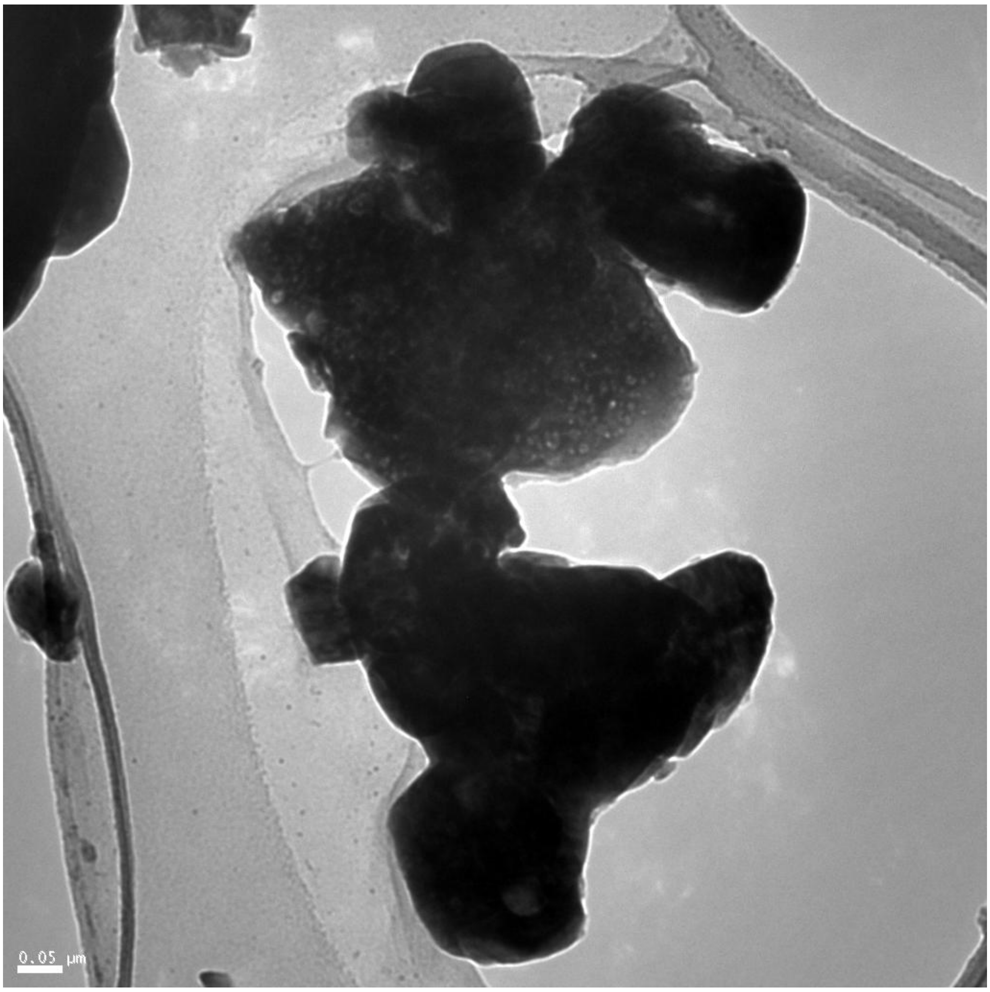

Figure S13. TEM image of fresh Ag-W catalyst prepared by conventional impregnation method.

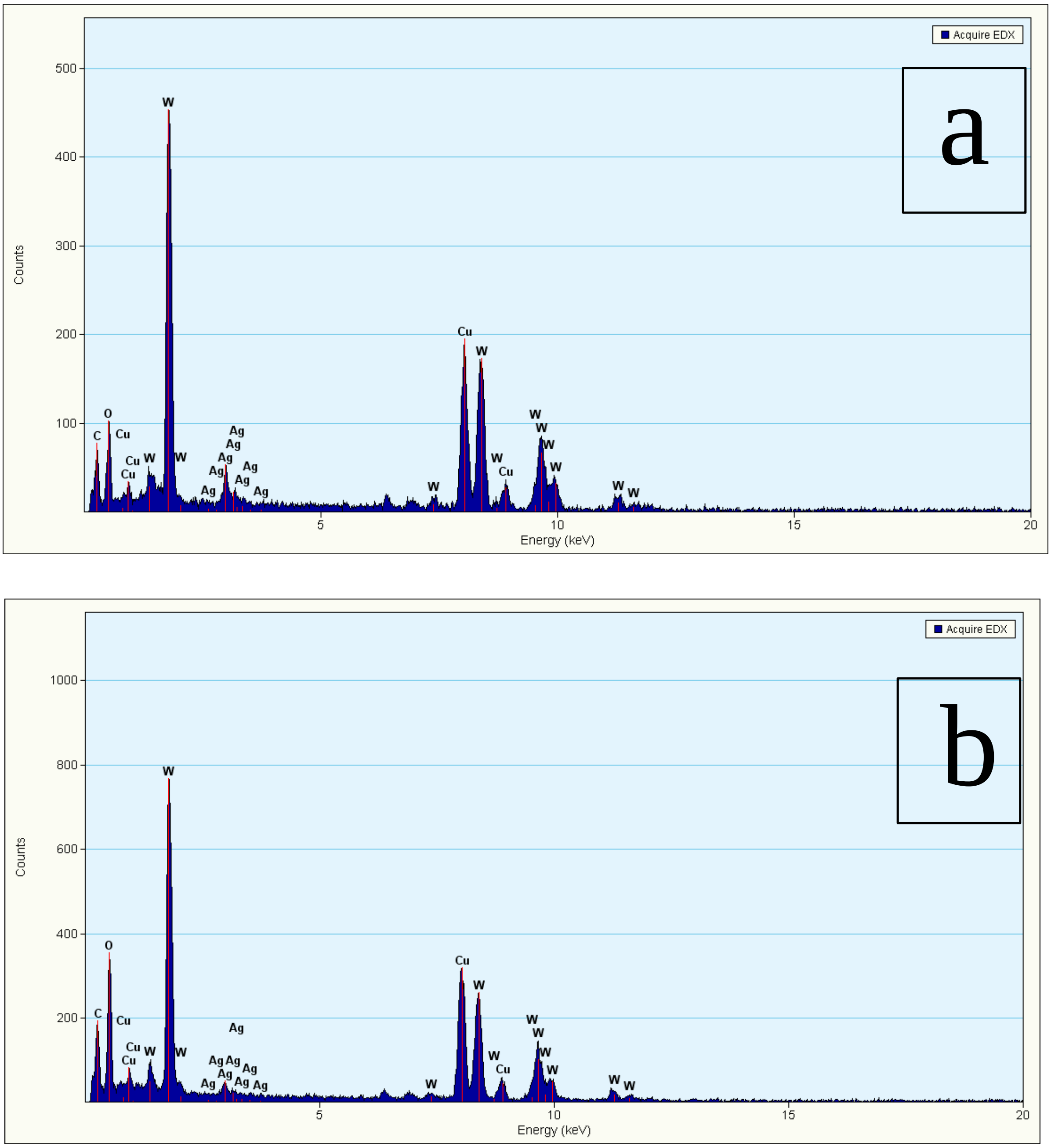

Figure S14. TEM-EDAX of (a) fresh and (b) spent Ag-W alovera-like catalyst.

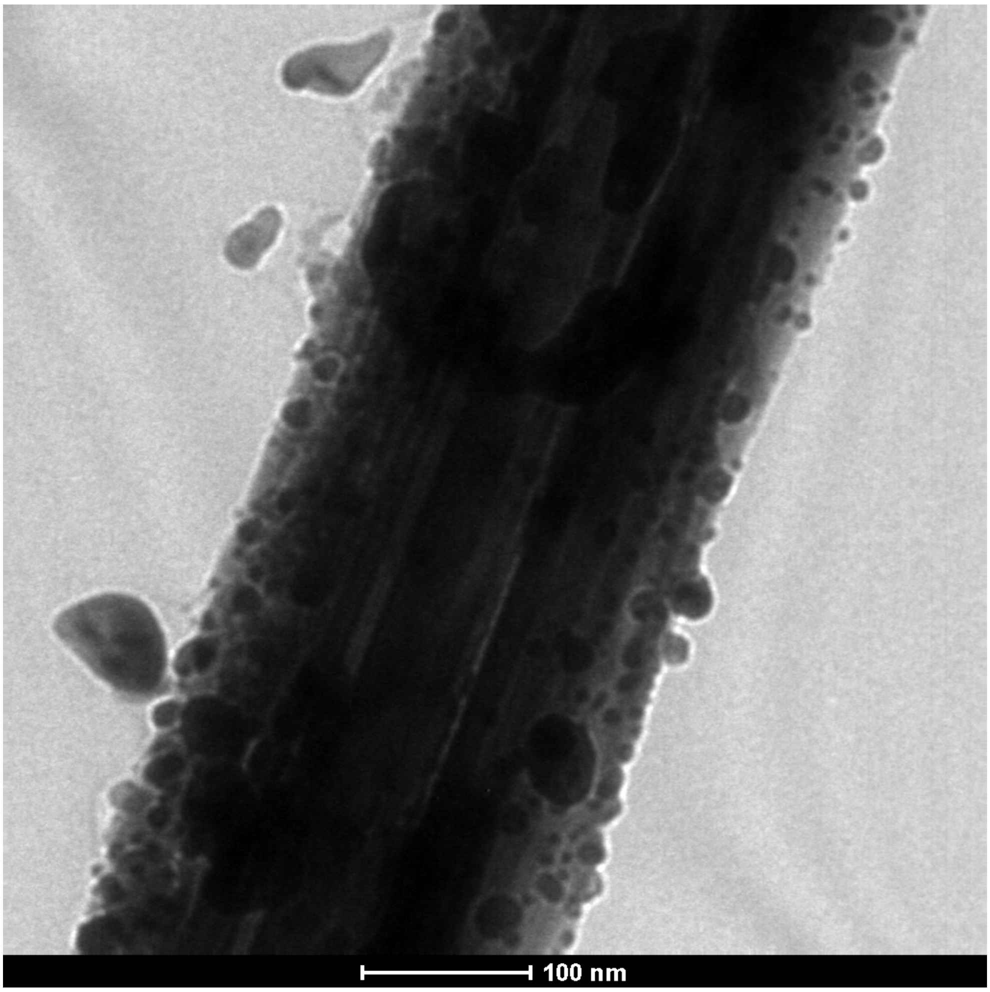

Figure S15. TEM diagram of the Ag-WO_3 catalyst (with 5.8% Ag loading).

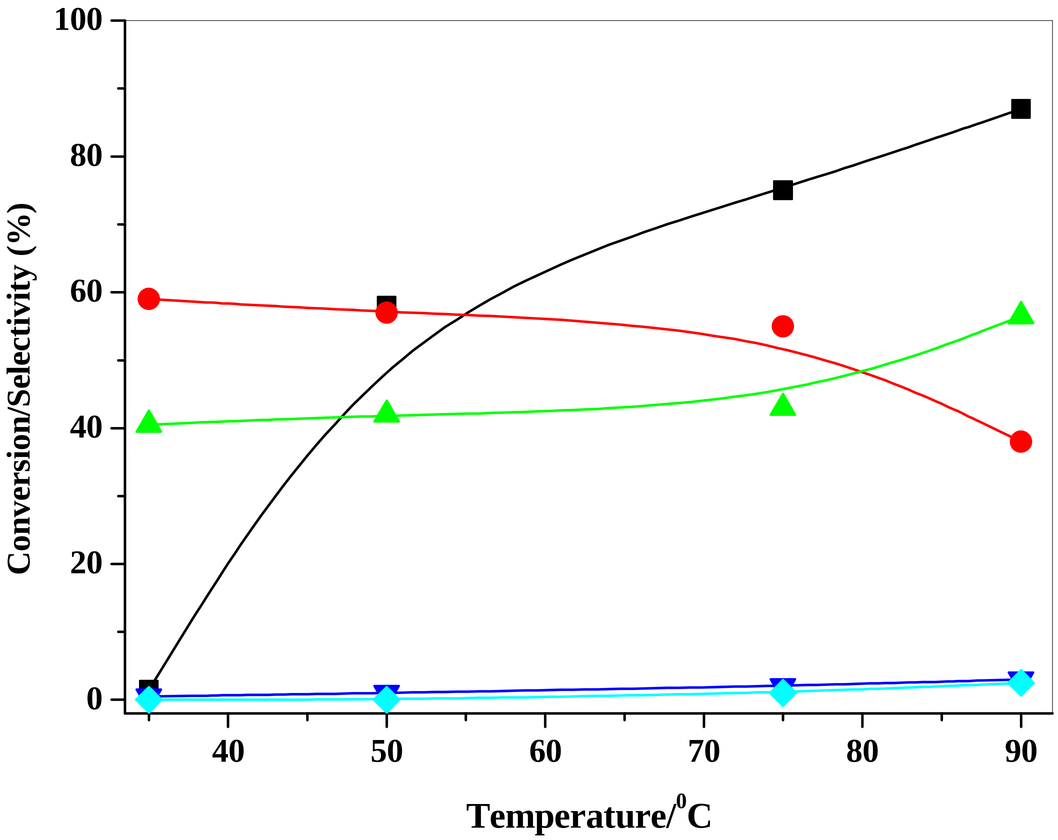

Figure S16. Effect of temperature on styrene oxidation.
[■] Conversion of styrene; [●] Selectivity to styrene oxide; [▲] Selectivity to benzaldehyde; [▼] Selectivity to phenylacetaldehyde [♦]Selectivity to benzoic acid.
Reaction Condition: styrene =1g; catalyst = 0.075g; styrene: H_2O_2 mole ratio =1:4; time = 12 h.

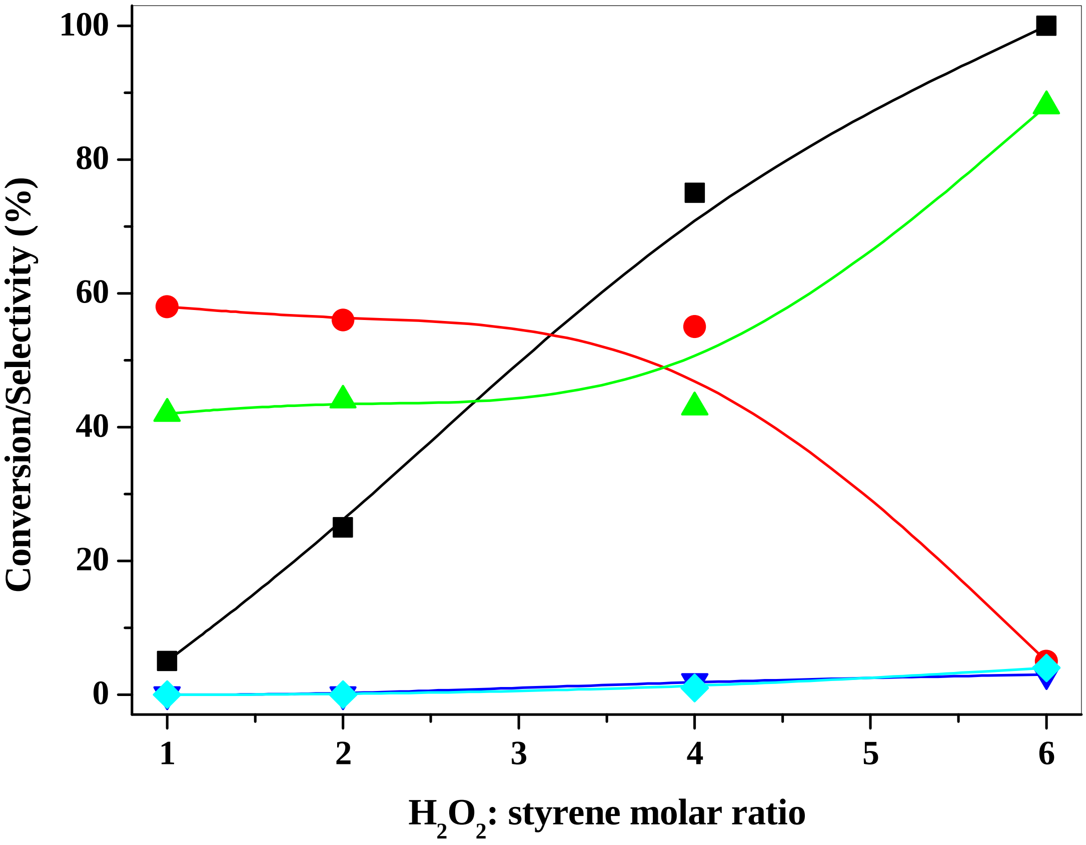

Figure S17. Effect of H_2O_2: styrene molar ratio on styrene oxidation.
[■] Conversion of styrene; [●] Selectivity to styrene oxide; [▲] Selectivity to benzaldehyde;
[▼] Selectivity to phenylacetaldehyde [♦]Selectivity to benzoic acid.
Reaction Condition: styrene =1g; catalyst = 0.075g; temperature = 75° C; time= 12 h.

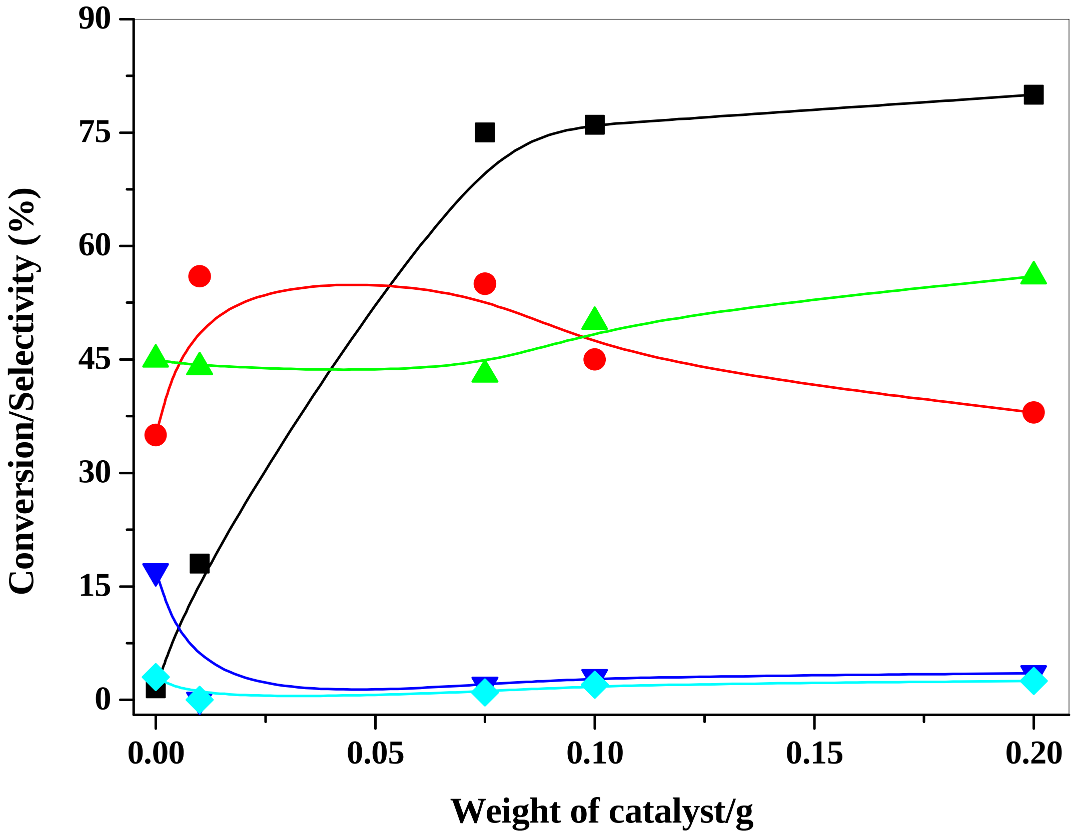

Figure S18. Effect of catalyst weight on styrene oxidation.

[■] Conversion of styrene; [●] Selectivity to styrene oxide; [▲] Selectivity to benzaldehyde; [▼] Selectivity to phenylacetaldehyde [♦]Selectivity to benzoic acid.

Reaction Condition: styrene =1g; styrene: H_2O_2 mole ratio =1:4; temperature = 75° C; time= 12 h.

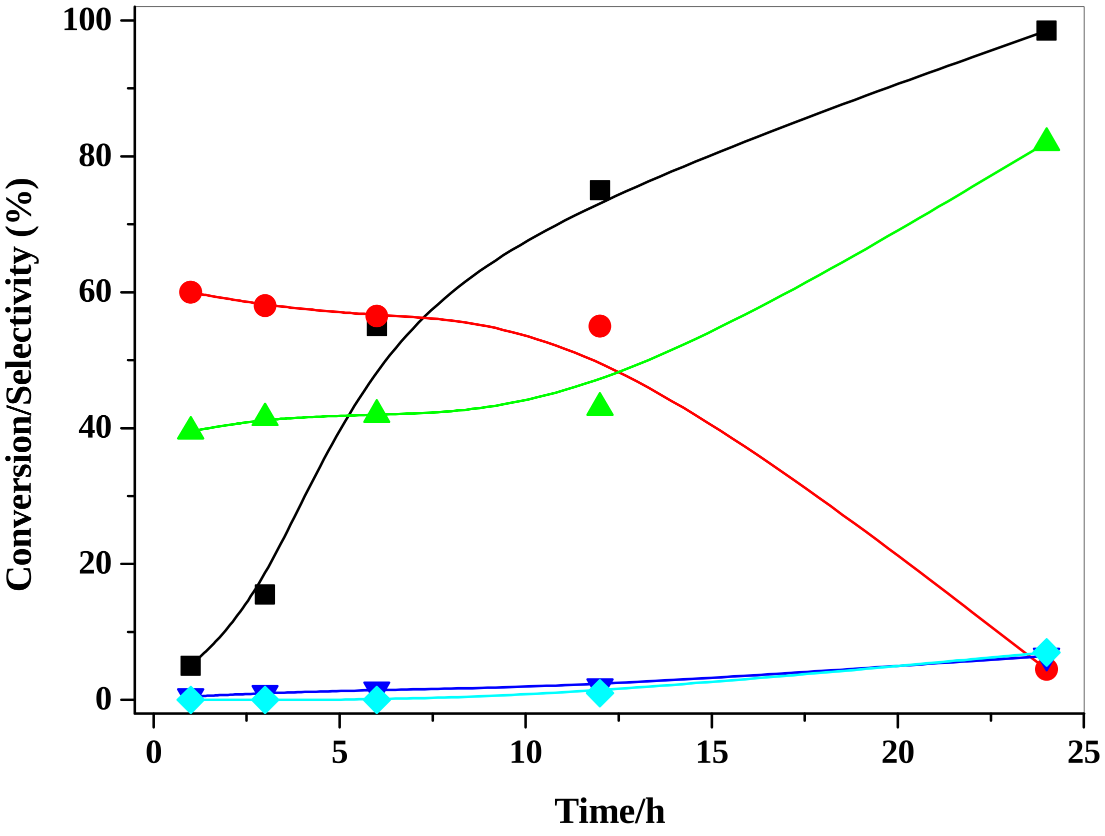

Figure S19. Effect of time on styrene oxidation.

[■] Conversion of styrene; [●] Selectivity to styrene oxide; [▲] Selectivity to benzaldehyde; [▼] Selectivity to phenylacetaldehyde [♦]Selectivity to benzoic acid.

Reaction Condition: styrene =1g; catalyst = 0.075g; styrene: H_2O_2 mole ratio =1:4; temperature = 75° C.

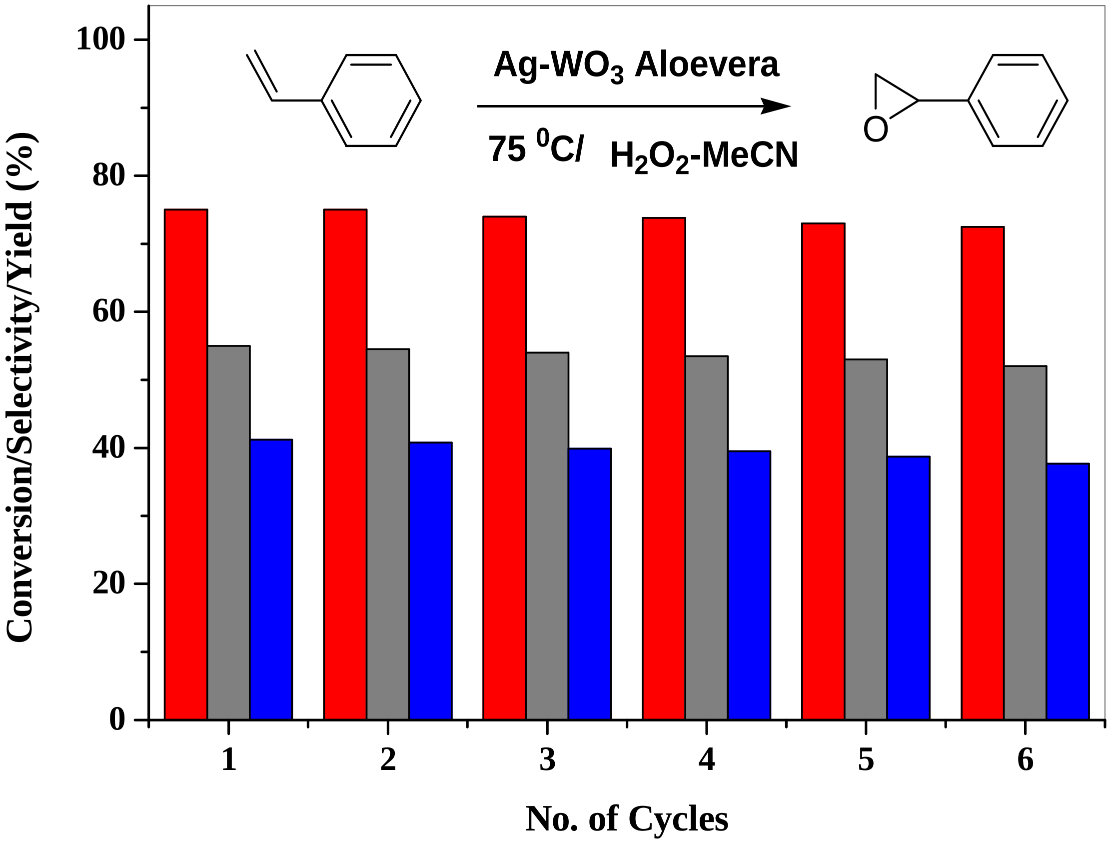

Figure S20. Reusability test on styrene oxidation.

[🟥] Conversion of styrene; [■] Selectivity to styrene oxide; [🟦] Yield of styrene oxide. Reaction Condition: styrene =1g; catalyst = 0.075g; styrene: H_2O_2 mole ratio =1:4; temperature = 75° C; time = 12h.

Scheme S1. Plausible mechanism for the formation of styrene oxide and benzaldehyde.