

ARTICLE

### Electronic Supplementary Information (ESI)

#### ESI-1: Experimental methods and Reactor Setup:

Powder XRD pattern of materials were collected from PANalytical X'pert Pro dual goniometer diffractometer. The radiation used was Cu K $\alpha$  (1.5418 Å) with Ni filter and the data collection was carried out using a sample holder in Bragg-Brentano geometry. A proportional counter detector was used for low angle experiments. The data were collected with a step size of 0.02° and a scan rate of 0.5 °/min. The sample was spun slowly throughout the scan for better counting statistics.

Nitrogen adsorption/desorption isotherms for the materials were collected from Quantachrome autosorb automated gas sorption system (NOVA 1200). The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area from the desorption branch. The pore size distribution was calculated by analyzing the desorption branch of the nitrogen sorption isotherm using Barrett-Joyner-Hollenda (BJH) method.

A FEI TECNAI 3010 electron microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 Å) was used for recording High Resolution TEM of all materials. Samples were crushed and dispersed in isopropanol before depositing onto a holey carbon grid. TEM images were taken on T-30 FEI instrument. Energy Dispersive X-Ray (EDX) measurements were performed in SEM system (FEI, Model Quanta 200 3D) equipped with EDX attachment. EDX spectra were recorded in the spot-profile mode by focusing the electron beam onto specific regions of the sample.

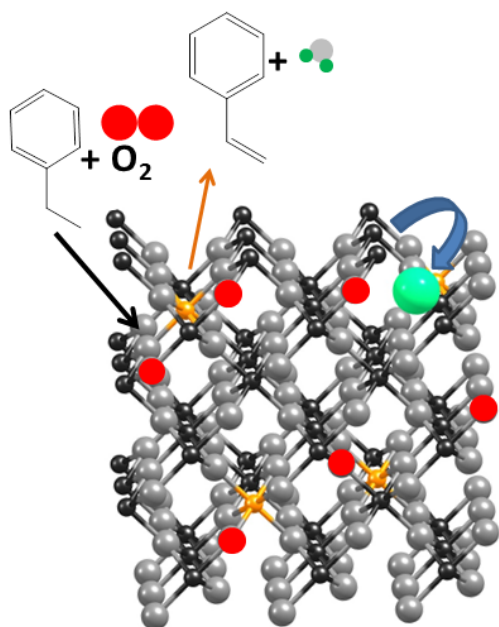
Raman spectra were recorded on a Horiba JY LabRAM HR 800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser source and a spectral resolution of 0.3 cm<sup>-1</sup>. Infrared spectroscopic studies were carried out on Bruker's ALPHA instrument using ECO ATR mode. IR analysis was carried on powdered samples.

#### Reactor and Reaction:

Reactor system was prepared via settling a column of ceramic beads where sieved catalysts bed (1 mL or

0.76±0.04 g) is placed in the middle of reactor with quartz wool packed in the spaces on either side of the bed. Prepared catalysts pellet of 0.8 mm mesh size were filled into the reactor. The temperature on the wall of the reactor and in the catalyst bed was measured using a K-type coaxially centered thermocouple. EB flow was controlled using a high precision isocratic pump (Lab Alliance Series II) and the oxygen flow was controlled using a Brooks-make mass flow controller (5890E series). The reactant flow was configured to operate in up-flow mode and the products were condensed using a chiller. Samples of reaction mixture were collected at regular interval via cold trap into vials; collected samples were then analyzed using an Agilent 6890N gas chromatograph with a BP-5 (5.5% phenyl methyl siloxane) column along with an FID detector. The optimized conditions for the reactions were: 500 - 530 °C, atmospheric pressure, LHSV (liquid hourly space velocity) 1.8 h<sup>-1</sup> with respect to EB, and air flow at GHSV (gas hourly space velocity) 10800 h<sup>-1</sup>, i.e. O<sub>2</sub>/EB molar ratio of 2.0. Liquid and gaseous products analysis was carried out separately and selectivity shown in all reaction results is for liquid products only. All data points were obtained in duplicate with an error of ± 2%.]. See DOI: 10.1039/b000000x/

## Graphical Abstract



Anatase- $\text{Mn}_x\text{Ti}_{1-x}\text{O}_2$  was converted to  $\text{Mn}_3\text{O}_4$  supported on rutile- $\text{TiO}_2$  under ODH of ethyl benzene to styrene at 500 °C, by utilizing lattice oxygen.