

Supporting Information

Indium oxide nanocluster doped TiO₂ catalyst for activation of molecular O₂

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Materials and Reagents

Titanium (IV) isopropoxide [Ti{OCH(CH₃)₂}₄, 95% Alfa aesar], Indium (III) chloride (InCl₃, anhydrous 99.99% Alfa Aesar), ethanol (Merck, anhydrous) and nitric acid (70% Merck) were used during synthesis. Titania nanoparticles (P-25, Aldrich) and Indium oxide nanoparticles (SRL, average particle size 50 nm) were used to r control experiments.

Synthesis of indium oxide nanoclusters doped TiO₂ (In₂O₃/TiO₂) nanostructures

In a typical optimized experimental procedure, 0.5 g of InCl₃ was added to 5 mL of ethanol and was stirred for 10 minutes at ambient conditions. To this 12.5 mL solution Titanium isopropoxide was added drop-wise under continuous stirring. After that 50 mL of 0.1 M HNO₃ is added to the reaction mixture. Then the temperature was raised to 80 °C and the suspension was heated for 2 h with continuous stirring in a closed vessel. Afterwords the mixture was transferred to an autoclave and kept in a furnace at 150 °C temperature for 24 h duration for crystallization under hydrothermal condition. After the hydrothermal treatment, autoclave was allowed to cool at room temperature and product was collected by vacuum filtration. Te residue was washed several times with distilled water, and finally dried at 80 °C for 12 h. The

$\text{In}_2\text{O}_3/\text{TiO}_2\{101\}$ and $\text{In}_2\text{O}_3/\text{TiO}_2\{001\}$ nanostructures were obtained by calcination of dry powder at 450 °C (10 °C min⁻¹) and 550 °C (10 °C min⁻¹) temperature for 2.5 h respectively. The $\text{In}_2\text{O}_3/\text{TiO}_2\{101\}$ refers to the sample with exposed {101} planes and $\text{In}_2\text{O}_3/\text{TiO}_2\{001\}$ refers to samples with some exposed {001} planes (in addition to predominant {101} plane).

Theoretical calculation method

All the calculations were performed using the Forcite anneal module in Materials Studio 7.0 molecular modeling software package (Accelrys). The Forcite anneal module is an advanced classical molecular mechanics calculation tool that can obtain geometry optimizations, energy calculations, and dynamic simulations reliably for a wide range of molecular and periodic systems. The geometry optimization process was carried out by using an iterative process, in which the atomic coordinates were adjusted until the total energy of a structure was minimized. Geometry optimization was based on reducing the magnitude of the calculated forces until they became smaller than defined convergence tolerances. Anneal model was specifically used to find the global minimum energy structures for molecules/surfaces under consideration, to carry out energy calculations. The temperature range used for annealing was 300K-500K. Anatase TiO_2 surface was cleaved to obtain TiO_2 {101} and TiO_2 {001} surfaces. After surface cleaving, some of the titania were capped with hydroxyl group arbitrarily. Periodicity of the structures was changed by constructing a super cell, and then vacuum slab of thickness 20 Å on TiO_2 {101} and TiO_2 {001} surfaces to eliminate the interaction between the neighbouring cells. Indium oxide unit cell (In_2O_3) was used as input component to construct Indium oxide nanocluster (1 nm) using build command. The structure was stabilized using Forcite anneal in the same temperature range (300K-500K), with universal forcefield component. Geometry optimised structures and corresponding energy minimised values for various structures such as indium oxide nanoclusters,

oxygen molecule, TiO₂ surfaces ({001} and {101}) and all feed components used for calculations are given in Table S1. Adsorption locator module was used to find the specific location of In₂O₃ nanoparticle, its adsorption energy, and density field across TiO₂ {001} and {101} surfaces. Adsorption Locator identifies possible adsorption configurations by carrying out Monte Carlo searches of the configurational space of the substrate-adsorbate system as the temperature is slowly decreased. In both approaches (Forcite anneal and Adsorption Locator) the final temperature was taken 150°C (423K), in accordance with the experimental reaction temperature. Similar approach was used to find the adsorption characteristics of feed (Styrene: Oxygen 1:20) and product (Styrene epoxide and benzaldehyde) on both surfaces (In₂O₃ doped TiO₂ {001} and In₂O₃ doped {101} surfaces). Adsorption energy and isosteric heat of adsorption for individual component was also calculated.

Measurement and Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on Bruker D8 Advance Diffractometer operating in the reflection mode with Cu-K α radiation (40 KV, 40 mA). Field Emission Gun Transmission Electron Microscope JEOL-TEM-2010, operating at 200 kV was used for high-resolution transmission electron microscope (HRTEM) images. X-ray photoelectron spectroscopy was performed on Axis-Ultra DLD, Shimadzu Instrument equipped with an Mg K α X-ray exciting source with 30 mA current, 15 kV voltage, and 80 eV pass energy. The energy scale was calibrated using Au. The Brunauer-Emmett-Teller (BET) specific surface areas were obtained from the N₂ adsorption/desorption isotherms recorded on BELSORP max (Japan) at -196 °C. The samples were degassed and dried under a vacuum system at 150 °C for 2-3 h prior to the measurement.

Catalytic activity measurement

The reaction mixture was prepared by using 10 mL DMF (99.8 %, Merck, India), 6.5 mmol styrene (99 %, Acros Organics) and 0.1 mL dodecane (99 %, Acros Organics) as an internal standard. The reaction mixture was shaken vigorously for homogenization and 0.1 g catalyst was added to it. Now the prepared reaction mixture along with catalyst was kept in a batch reactor where 50 mL two necked round bottom flask was fitted with a water condenser maintained at a constant temperature (150 °C). Thereafter oxygen (99.99 % purity) was bubbled into the mixture at the flow rate of 10 mL/min (flow is maintained by Aalborg mass flow controller; USA) with continuous stirring (700 rpm) condition. The reaction mixture was analyzed by GC-1000 (Chemito-India) equipped with SE-30 column and FID detector. The TOF was calculated on the basis of moles of styrene converted/mol of indium present in the catalyst per hour. The Conversion profile for predicted reaction order was verified using COMSOL multiphysics software.

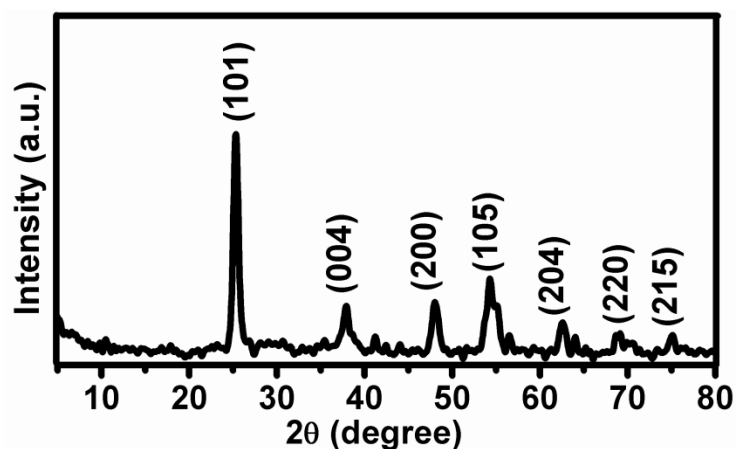


Fig. S1: XRD pattern of 1% In₂O₃/TiO₂ calcined at 550°C temperature

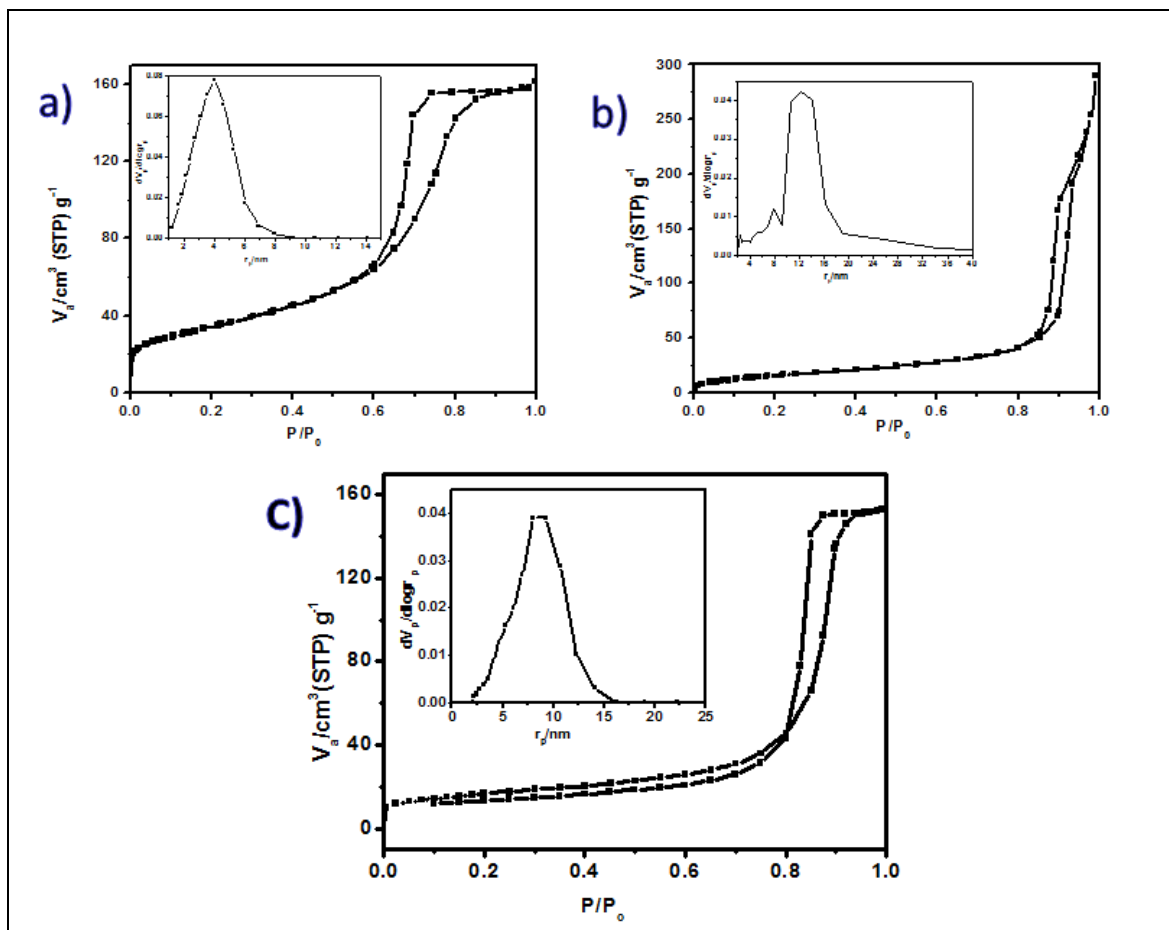
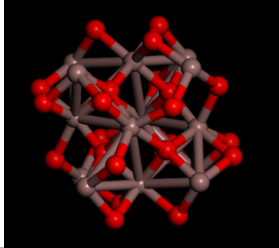
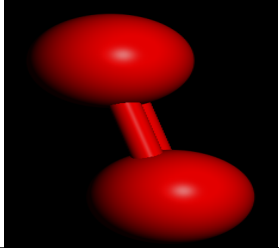
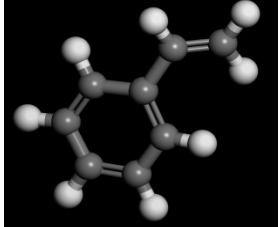
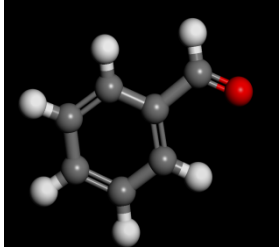
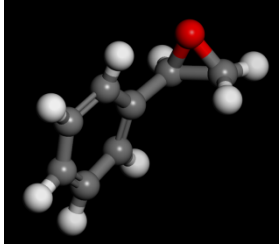


Fig. S2 N₂ Physisorption results of a) 1 at% In/TiO₂ calcined at 450 °C b) 1 at% In/TiO₂ calcined at 550 °C c) 2 at% In/TiO₂ calcined at 550 °C

The complete computational details:

Table S1 Global minimum energy structures and energy details of input structures used for oxygen and styrene activity calculations.

Structure	Method used	Final Energy of the structure kcal/mol	Final stable Structure
In ₂ O ₃ nanoparticle (1 nm)	Forcite anneal	5126.487	
Oxygen molecule	Forcite anneal	3.837	
Styrene	Forcite anneal	46.118	
Benzaldehyde	Forcite anneal	38.101	
Styrene oxide	Forcite anneal	385.674	

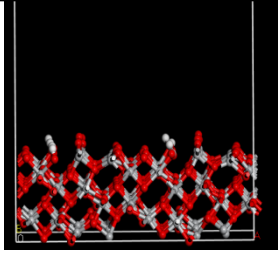
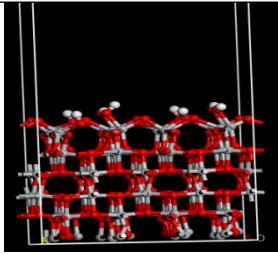
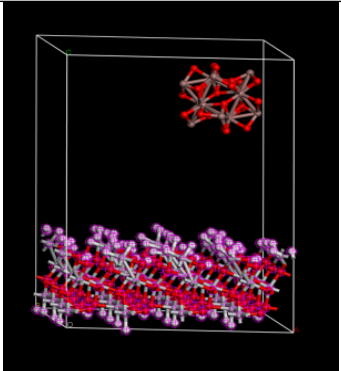
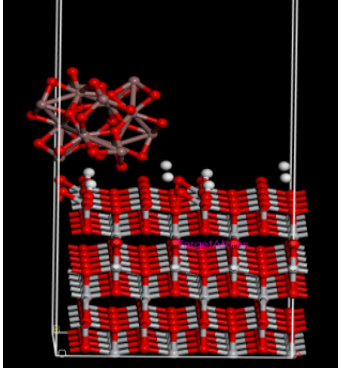
TiO₂ anatase 101 surface	Forcite anneal	Total enthalpy :8728.478 kcal/mol Total energy :12130.745 kcal/mol	
TiO₂ anatase 001 surface	Forcite anneal	Total enthalpy :12418.063 kcal/mol Total energy 13677.986 kcal/mol	

Table S2 Calculation of adsorption energy of final structures after indium oxide adsorbed on different TiO₂ surfaces.

Structure	Method used	Final Energy of the structure kcal/mol	Final stable Structure
In ₂ O ₃ nanoparticle (1 nm) on TiO ₂ anatase 101 surface	Adsorption locator calculation, Task : simulated annealing Forcefield: universal Electrostatic: Group based	5079.103	
In ₂ O ₃ nanoparticle (1 nm) on TiO ₂ anatase 001 surface	Adsorption locator calculation, Task : simulated annealing Forcefield: universal Electrostatic: Group based	5087.164	

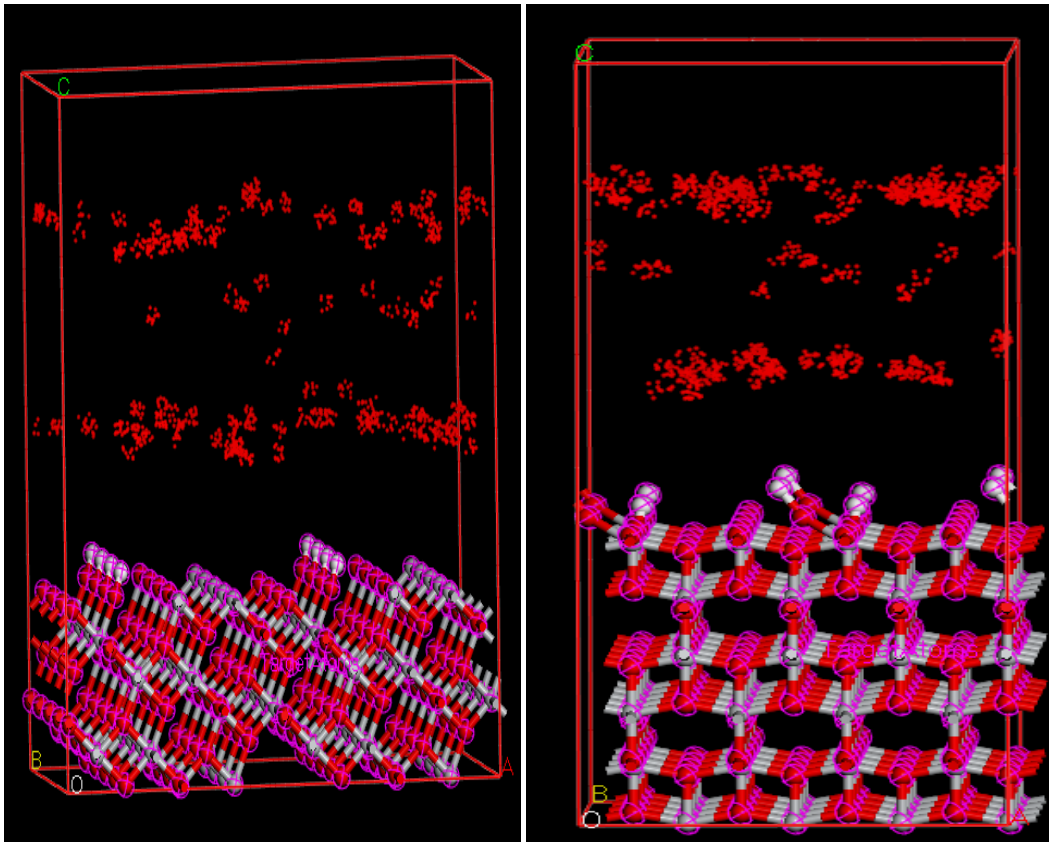


Fig. S3 In_2O_3 nanoparticle (1 nm) Fields on TiO_2 anatase 101 surface and 001 surface.

A. Formula used to calculate Binding energy for In_2O_3 :

$$E(\text{In}_2\text{O}_3\text{-TiO}_2(101 \text{ or } 001)) - E(\text{In}_2\text{O}_3) - E(\text{TiO}_2(101 \text{ or } 001) \text{ surface})$$

B. Formula used to calculate Binding energy for feed (styrene and oxygen):

$$E \text{ final structure} - (20 * E_{\text{O}_2} + E_{\text{styrene}} + E_{\text{In}_2\text{O}_3\text{-TiO}_2(101 \text{ or } 001)})$$

C. Formula used to calculate Binding energy for products ((styrene and oxygen):

$$E \text{ final structure} - (E_{\text{O}_2} + E_{\text{styrene}} + E_{\text{In}_2\text{O}_3\text{-TiO}_2(101 \text{ or } 001)})$$

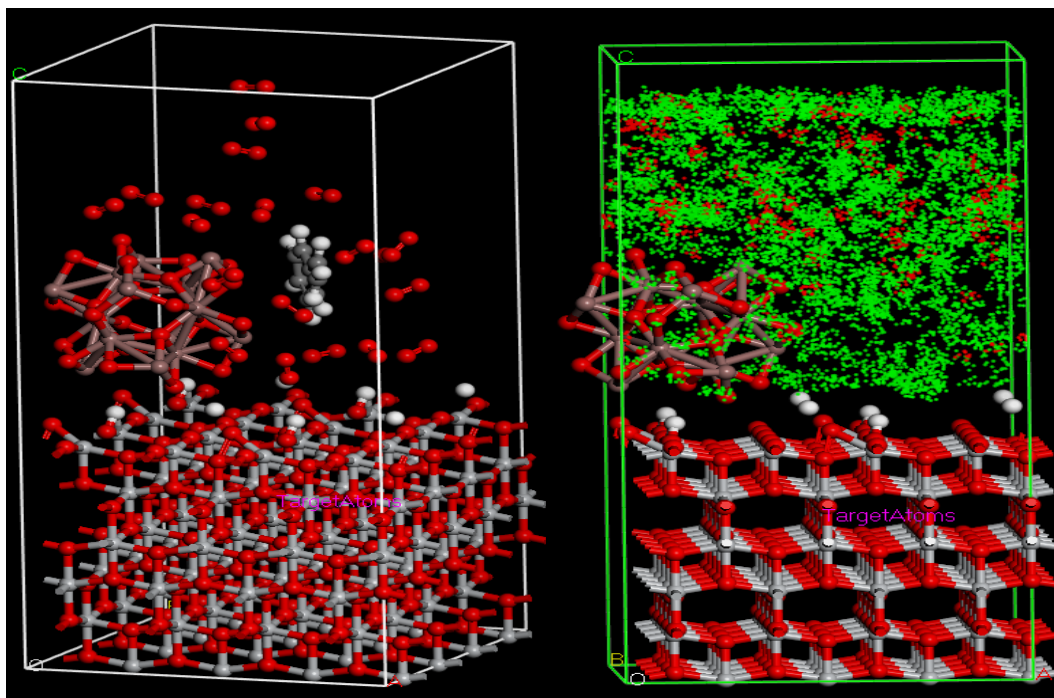


Fig. S4 (a) Geometry optimized structure showing adsorption of Styrene and oxygen (1 molecule styrene and 20 molecules O₂, the ratio selected for computational studies is in accordance with experimental conditions used in our work) on In₂O₃-TiO₂ 101 surface (b) field density distribution; (Green=oxygen density, red=styrene density).

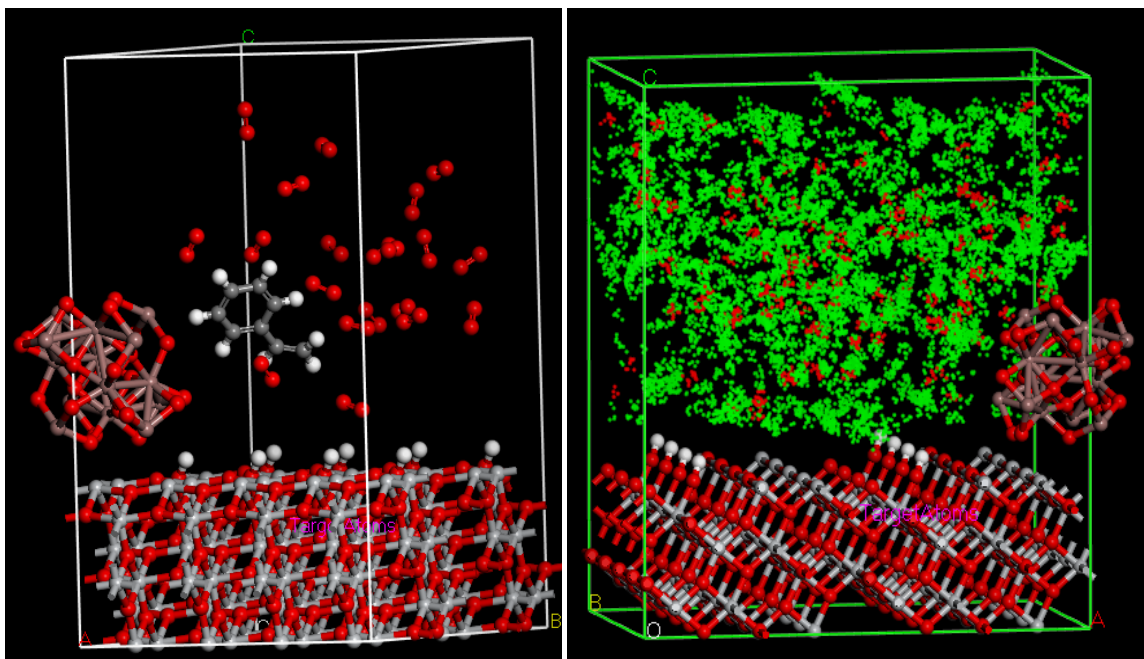


Fig. S5 (a) Geometry optimized structure showing adsorption of Styrene and oxygen (1 molecule styrene and 20 molecules O₂, the ratio selected for computational studies is in accordance with experimental conditions used in our work) on In₂O₃-TiO₂ 001 surface (b) field density distribution; (Green=oxygen density, red=styrene density).

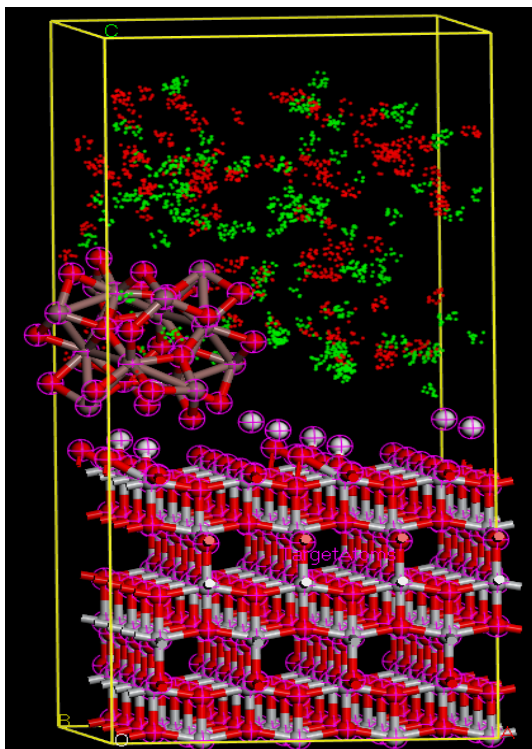


Fig. S6 Benzaldehyde and styrene epoxide (products) adsorption on In₂O₃-TiO₂ 001 surface (catalyst); final structure and filed (Red= Styrene epoxide density, Green= benzaldehyde density).

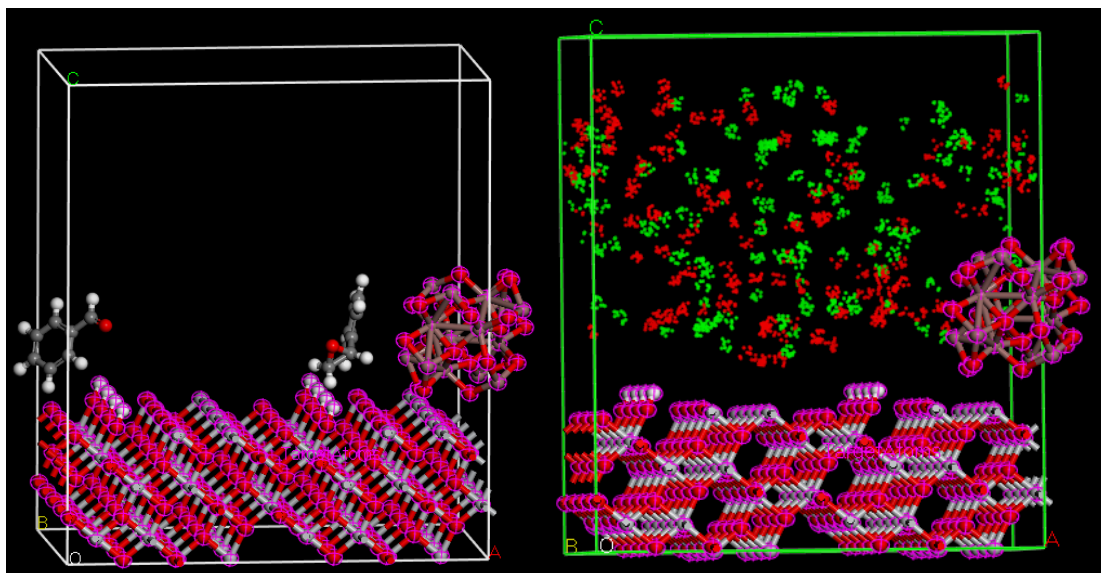


Fig. S7 Benzaldehyde and styrene epoxide (products) adsorption on In₂O₃-TiO₂ 101 surface (catalyst); final structure and filed (Red= benzaldehyde density, Green= Styrene epoxide density).

Table S3 Isothermic heat and Energy for Adsorption of feed and products on two surfaces of In₂O₃-TiO₂ (001) and (101) phases

	In ₂ O ₃ -TiO ₂ (101) surface		In ₂ O ₃ -TiO ₂ (001) surface	
Isothermic heat and Energy for Adsorption of feed on two surfaces				
	Isothermic heats kCal/mol	Average total energy kcal/mol	Isothermic heats kCal/mol	Average total energy kcal/mol
Oxygen	6.512	91.213	7.078	83.047
Styrene	20.779		24.306	
Isothermic heat and Energy for Adsorption of products on two surfaces				
	Isothermic heats kCal/mol	Average total energy kcal/mol	Isothermic heats kCal/mol	Average total energy kcal/mol
benzaldehyde	20.333	394.011	23.614	390.438
styrene oxide	34.372		36.950	

Table S4 Order and rate constant determination (over catalyst calcined at 450°C)

Order (n)	A	Rate constant, k hr ⁻¹	R ²
0	$(N_{styrene0} - N_{styrene})$	0.188	0.908
1	$\ln(N_{styrene0}/N_{styrene})$	0.032	0.876
2	$1/(N_{styrene0} - N_{styrene})$	0.005	0.838

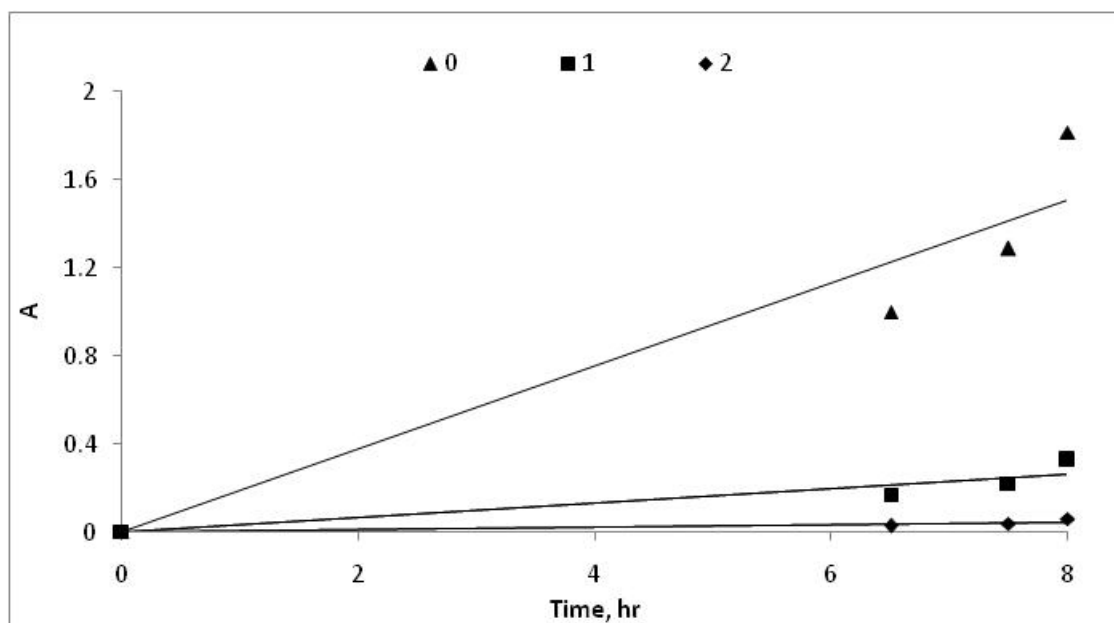


Fig. S8 Plot of A vs. Time (h) for styrene oxidation reaction in a batch reactor for styrene oxidation in a batch reactor at 150 °C (over catalyst calcined at 450 °C)

Table S5 Order and rate constant determination (over catalyst calcined at 550 °C)

Order (n)	A	Rate constant, k hr ⁻¹	R ²
0	$(N_{styrene0} - N_{styrene})$	0.366	0.920
1	$\ln(N_{styrene0}/N_{styrene})$	0.073	0.835
2	$1/(N_{styrene0} - N_{styrene})$	0.015	0.728

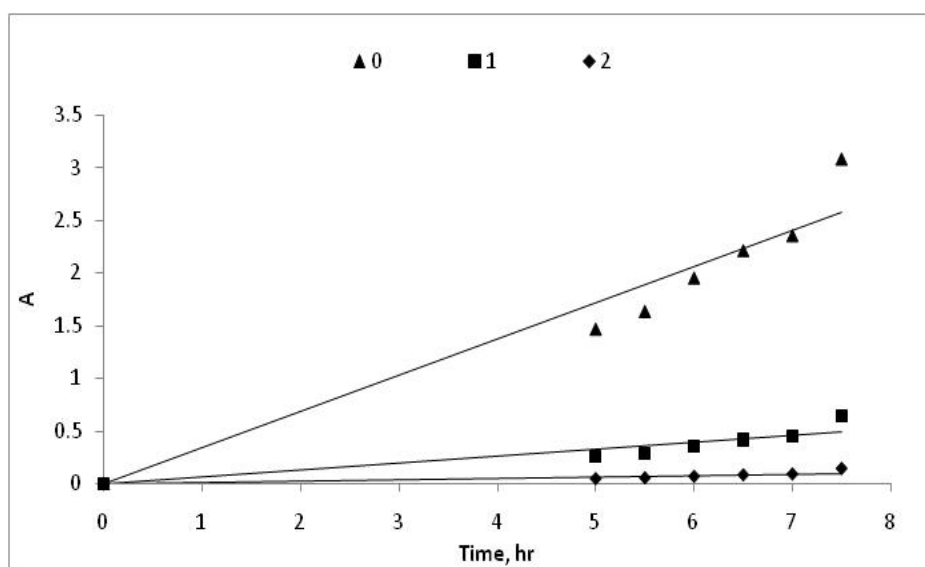
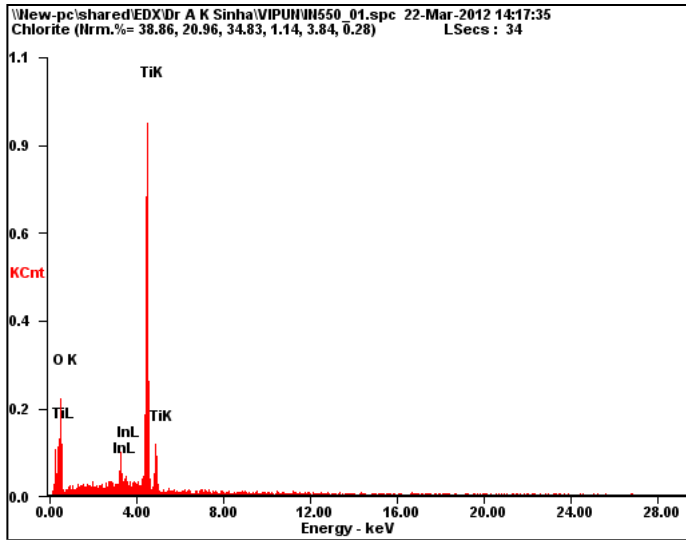


Fig. S9 Plot of A vs. Time (h) for styrene oxidation reaction in a batch reactor for styrene oxidation in a batch reactor at 150 °C (over catalyst calcined at 550 °C)

Fig. S10 EDX results of 1% In₂O₃/TiO₂



<i>Element</i>	<i>Wt %</i>	<i>At %</i>
<i>O K</i>	57.11	81.14
<i>In L</i>	05.41	01.07
<i>Ti K</i>	37.48	17.78

EDAX ZAF QUANTIFICATION STANDARDLESS SEC TABLE :
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