Electronic Supplementary Information

CeO_2 nano-wires with high aspect ratio and excellent catalytic activity for selective oxidation of styrene by molecular oxygen

Provas Pal,[a] *Sandip Kumar Pahari,*[a] *Apurba Sinhamahapatra,*[a] *Muthirulandi Jayachandran,*[b] *G. V. Manohar Kiruthika,*[b] *Hari C. Bajaj,*[a] *and Asit Baran Panda* [a, c] *

[a] *Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR), G.B. Marg, Bhavnagar-364002, Gujarat, India. Fax: +91-2782567562; Tel: +91-2782567760 Ext. 704; E-mail: abpanda@csmcri.org.*

[b] *Electrochemical Materials Science Division, Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, India.*

[c] *Central Glass & Ceramic Research Institute (CSIR), Raja SC Mullick Road, Kolkata-32, West Bengal, India.*

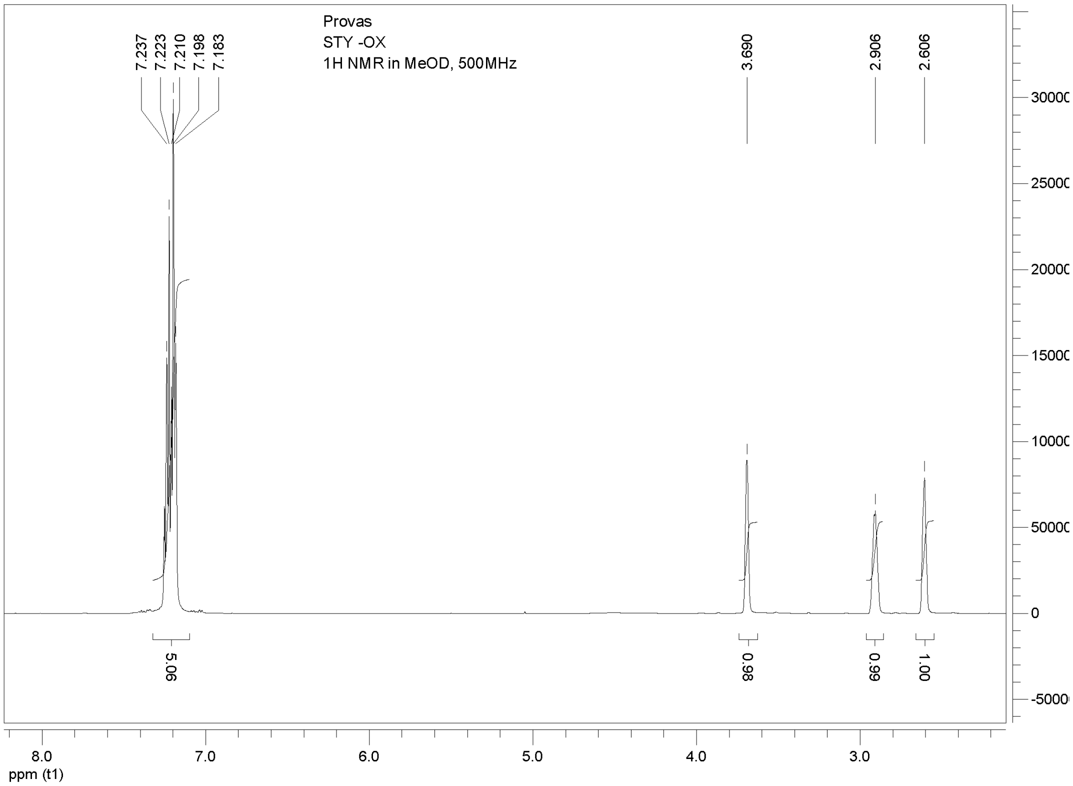
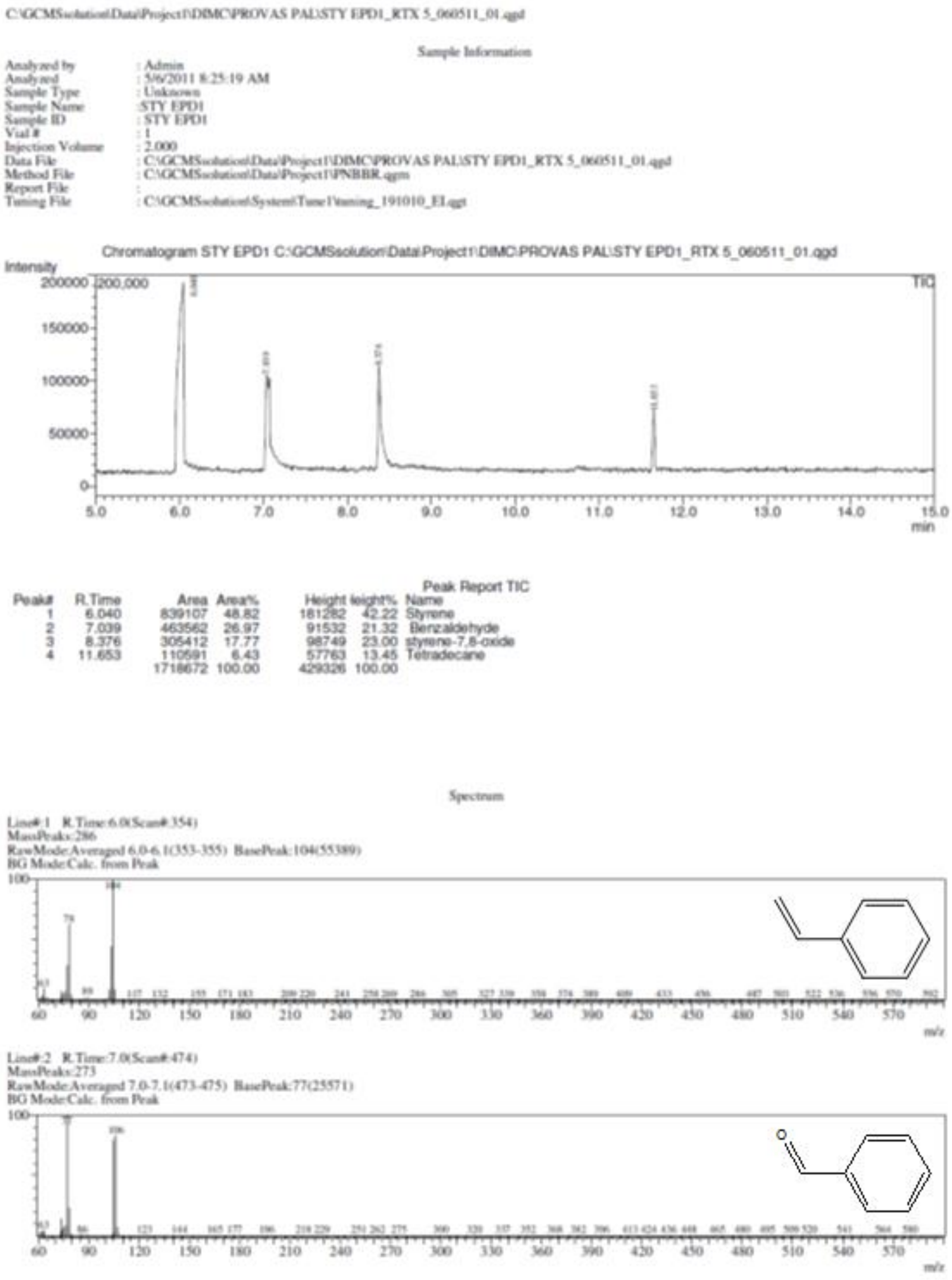


Fig. S1. ^{1}H NMR Spectrum for separated styrene oxide.

Styrene oxide ^{1}H NMR (MeOD, 500 MHz) δ (ppm) **:** 7.18-7.23 (m, 5H), 3.68 (dd, 1H, H1), 2.90 (dd, 1H, H2*trans*), 2.60 (dd, 1H, H2*cis*).



C:\GCMSsolution\Data\Project1\DIMC\PROVAS PAL\STY EPD1_RTX 5_060511_01.qgd

Sample Information

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Sample Type : Unknown
Sample Name :STY EPD1
Sample ID : STY EPD1
Vial # : 1
Injection Volume : 2.000
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Chromatogram STY EPD1 C:\GCMSsolution\Data\Project1\DIMC\PROVAS PAL\STY EPD1_RTX 5_060511_01.qgd

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	leight%	Name
1	6.040	839107	48.82	181282	42.22	Styrene
2	7.039	463562	26.97	91532	21.32	Benzaldehyde
3	8.376	305412	17.77	98749	23.00	styrene-7,8-oxide
4	11.653	110591	6.43	57763	13.45	Tetradecane
		1718672	100.00	429326	100.00	

Spectrum

Line#:1 R.Time:6.0(Scan#:354)
MassPeaks:286
RawMode:Averaged 6.0-6.1(353-355) BasePeak:104(55389)
BG Mode:Calc. from Peak

Line#:2 R.Time:7.0(Scan#:474)
MassPeaks:273
RawMode:Averaged 7.0-7.1(473-475) BasePeak:77(25571)
BG Mode:Calc. from Peak

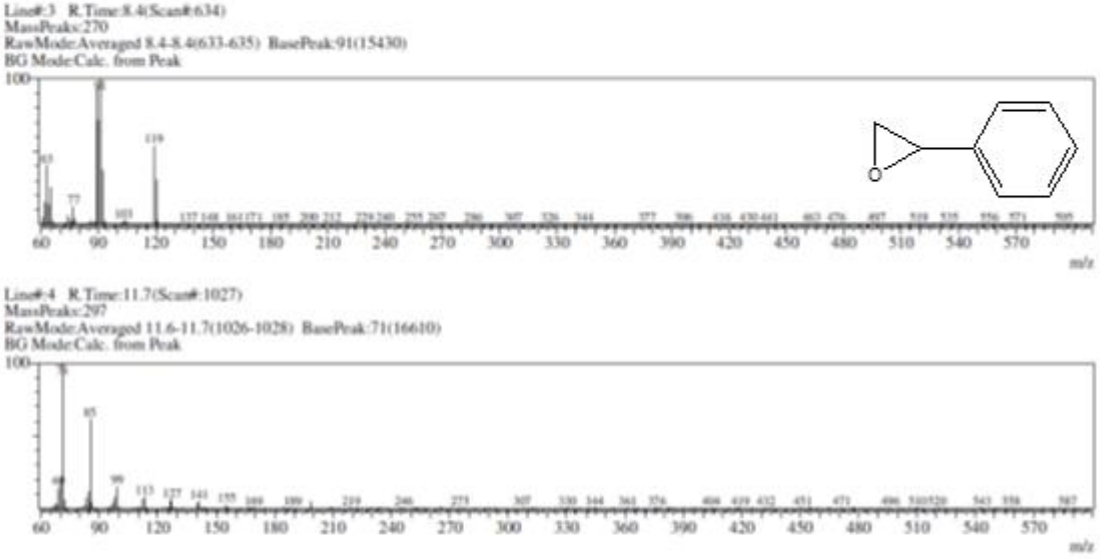


Fig. S2. GC-MS result for the reaction mixture of styrene, styrene oxide and benzaldehyde.

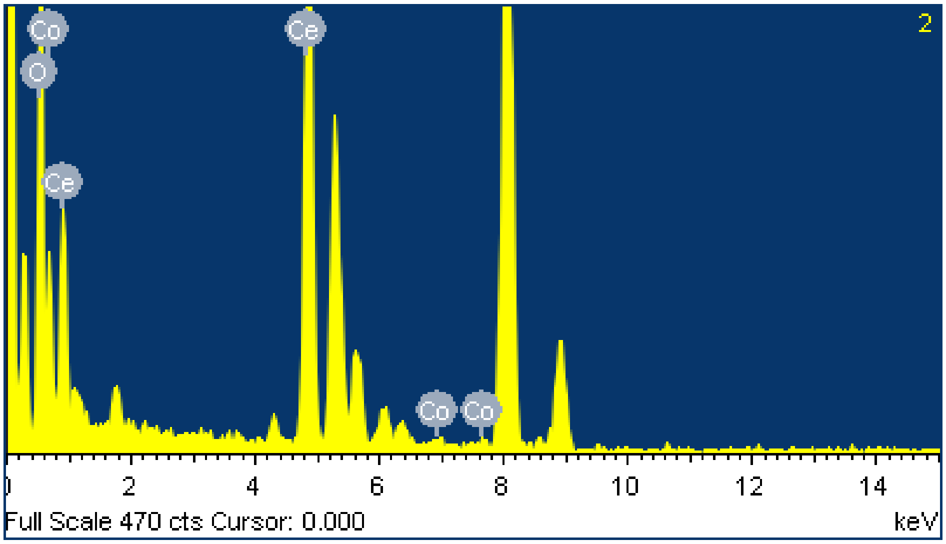


Fig. S3. EDX spectra of 2.5Co-CeO$_2$ NW.

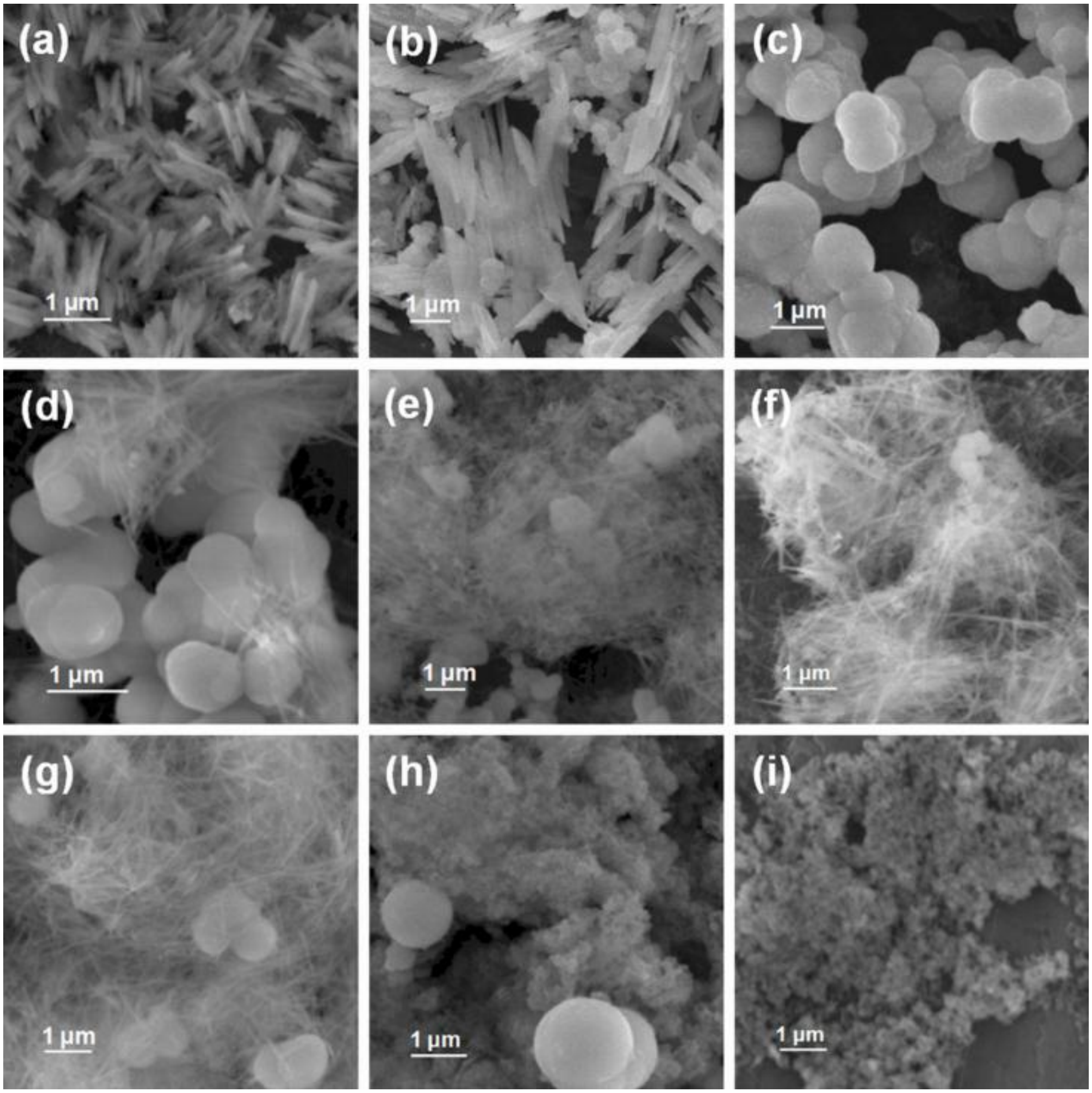


Fig. S4. SEM images of as-synthesized CeO_2 shapes using metal to ammonium carbonate ratio (w/w) of 1:3 (a) and 1:9 (b), using metal to PEG-600 ratio (w/v) 1:0 (c), 1:2.5 (d), 1:5 (e), 1:7.5 (f), using PEG-1000 (g), PEG-1500 (h) and sodium carbonate (i) at 150 °C in hydrothermal condition keeping all other conditions constant (metal : ammonium carbonate :: 1:6, metal : PEG ::1:10).

The described CeO_2 NW was selectively synthesized in hydrothermal condition at 150 °C using PEG-600 with a $(NH_4)_2Ce(NO_3)_6$ to PEG ratio of 1:10 (w/v) and $(NH_4)_2Ce(NO_3)_6$ to ammonium carbonate ratio of 1:6 (w/w). We have also synthesized CeO_2 of different morphology using the developed procedure by varying the amount of PEG, molecular weight of PEG, amount of ammonium carbonate and type of carbonate source (sodium carbonate instead of ammonium carbonate). Rods of different width leading to different kind of assembly were observed on variation of ammonium carbonate amount. Spindle like assembled rods of 0.8-2 μm length with ~50 nm width was produced using 3 g of ammonium carbonate instead of 6 g, keeping all other parameters unchanged (Fig. S4a). Whereas, assembled rods with ~125 nm width and 0.8-12 μm long was resulted on utilization of 9 g of ammonium carbonate (Fig. S4b). The amount of PEG has also a definite effect on the morphology.

Spherical CeO_2 particles with smooth surface were obtained in the absence of PEG (Fig. S4c). The formation of one dimensional structure (rod/wire) took place with the addition of PEG and as the amount of PEG is increased in the reaction system the formation of spherical particles decreased gradually (Fig. S4d-f). Again, with the increase of molecular weight of PEG the tendency of formation of 1D structure decreased. When the PEG-1000 was used instead of PEG-600, it resulted mixture of wires and spherical particles, whereas PEG-1500 did not produce any 1D structure and only mixture of spherical and teased cotton like particles (Fig. S4g-h) were obtained. Sodium carbonate gave only very small agglomerated particle. It was observed that the morphology of all the as-synthesized particles retained after calcinations at 500 °C.

As PEG is the main controlling factor for the synthesis of wires, so in the presence of reduced amount of PEG it resulted a mixture of wire and spherical particle (Fig. 7 d-f); and with the increased amount of PEG, the formation of spherical particles reduces. In the presence of reduced amount of PEG, initially the formed nanoparticles binds on the surface of PEG chain and after saturation of PEG surface, the remaining nanoparticles agglomerates to give spherical particle. As the molecular weight of PEG increased, the steric hindrance increased in the PEG chains and resulted in the mixture of wire and spheres in PEG-1000. In the case of PEG-1500 the strong steric hindrance caused the fusion of nanoparticles which reduced the control over particle and resulted the mixture of spherical and teased cotton like particles. Similar phenomena has been reported in literature during the formation of ZnO nanowires.[1]

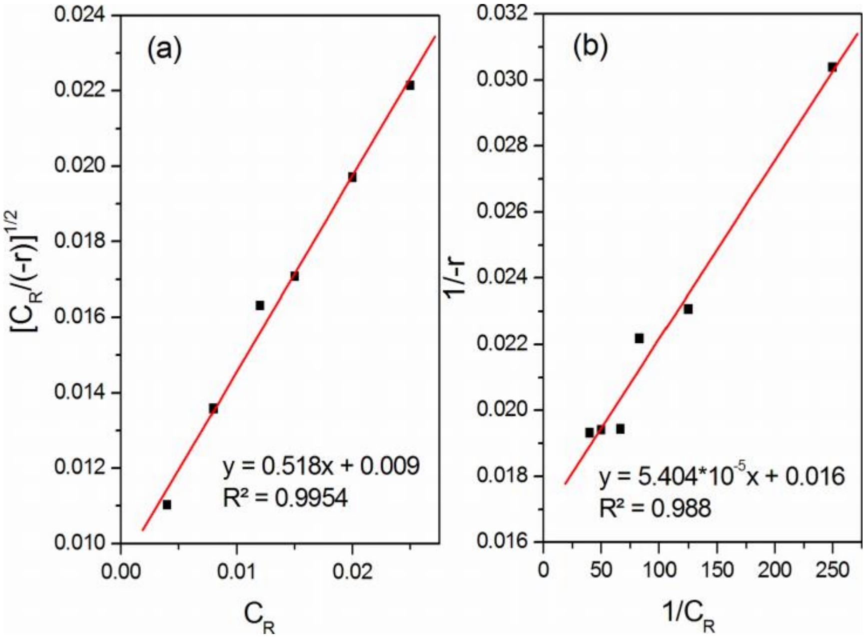
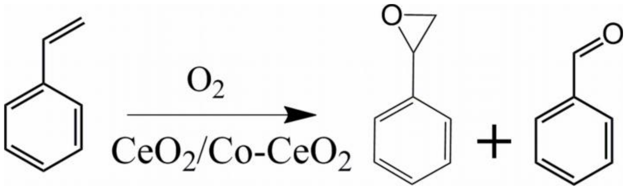


Fig. S5. Linear fitting of kinetic data for the Langmuir-Hinshelwood model(a) and Mars–van Krevelen model (b). Weight of catalyst =35 mg; DMF=15 mL; reaction temperature = 120°C.

In present work styrene oxidized by molecular oxygen in presence of CeO_2-NW based catalyst and reaction scheme is as follows:



For kinetic study, we have studied only the concentration of the styrene. We ignored the O_2 concentration, as we used a continues and constant flow of the O_2 hence the concentration of O_2 was much higher than other.

To understand the reaction mechanism, it is essential to identify the exact pathway which it follows. Among the several proposed model, Mars–van Krevelen (MvK) and Langmuir–Hinshelwood (LH) mechanisms are the mostly used for heterogeneously catalyzed oxidation reactions using molecular oxygen.

Evaluations of best fit for the kinetic models were made using rate expressions of the above mentioned model.

According Mars–van Krevelen model, the oxidation takes place through the lattice oxygen of catalyst surface and the reduced catalyst surface regenerate by molecular oxygen.

Equation of reaction through this model can be described as:

Organic molecule + Oxidized catalyst → Reduced catalyst + Products

Reduced catalyst + O_2 → Oxidized catalyst

The rate equation based on the above mechanism is expressed as:

$$-r = \frac{K_O K_R C_O C_R}{\alpha K_R C_R + K_O C_O}$$

Rearranged as:

$$\frac{1}{-r} = \frac{\alpha}{K_O C_O} + \frac{1}{K_R C_R}$$

Whereas K_R and K_O are the rate constant of the reactant and O_2 with catalyst .

In Langmuir–Hinshelwood model assumes that O_2 and organic molecules adsorb onto the same kind of active sites in non dissociative way. The rate expression based on this model is expressed as follows:

$$-r = \frac{k K_O K_R C_O C_R}{(1 + K_R C_R + K_O C_O)^2}$$

Rearranged as

$$\sqrt{C_R/(-r)} = \frac{1}{\sqrt{K_1}} + \frac{K_2}{\sqrt{K_1}} C_R$$

First we have plotted the time vs conversion of the reactant (mol %) up to 1 h and from tangent of the plot we got the **Initial rate**.

After that we plotted $C_R \; vs \sqrt{\frac{C_R}{-r}}$ (according to MvK model) and $1/C_R$ vs 1/-r (according to L-H model) and best linear fit was obtained according to L-H model. So we concluded that the reaction mechanism follows L-H model.

Table S1. Comparison of catalytic activity of the synthesized CeO_2 wire based catalysts and other literature reported results.

Sr. No.	Catalyst	Conversion	Selectivity	Yield*	Ref **
1	CeO_2-NW	80.5	70.1	56.4	Present investigation
2	**2.5%Co-CeO2-NW**	**97.5**	**74.2**	**72.34**	**Present investigation**
3	5%Co-CeO_2-NW	89.5	75.2	67.3	Present investigation
4	Co-ZSM-5	88.4	90.1	80.0	2
5	VO(acac:8-Q)-SBA-15	91.2	50.2	45.8	3
6	STA-12(Co)	98.5	21.0	20.68	4
7	CoAPO-5 molecular sieves	85	69	58.68	5
8	Co^{2+}SBA-15	93.9	65.5	61.5	6
9	Co-SBA-15_{20}	94.1	65.5	61.6	7
10	Cobalt substituted SSZ-51	50	75	37.5	8
11	nanosized Co_3O_4	81.1	84.0	68.2	9
12	$[Co(Bzo2[12]aneN_4)](ClO_4)_2$	41.9	47.6	20.0	10
13	Au_{55}-SiO_2	21.4	23.7	5.07	11
14	Co/Ts-1	94.5	74.3	70.1	12

* Theoretical yield: calculated from conversion and selectivity. ** Literature reported results.

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