Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Materials

TiO_2 supported Cobalt Oxide for Olefin Epoxidation Reaction – Characterization, Catalytic Activities and Mechanism – Using DFT Model

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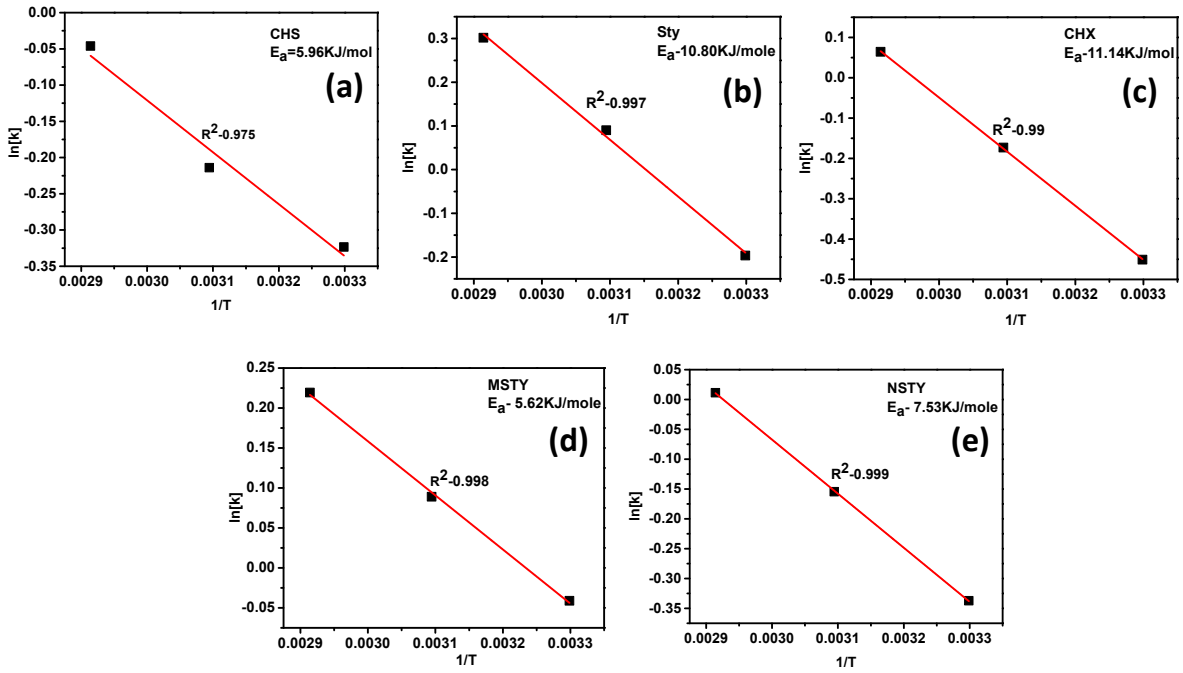


Fig. S1. Activation energy of (a)Chloro Styrene (b) Styrene (c) Cyclohexene (d) Methyl Styrene (e)Nitro Styrene.

Table S1. activation energy and rate constant.

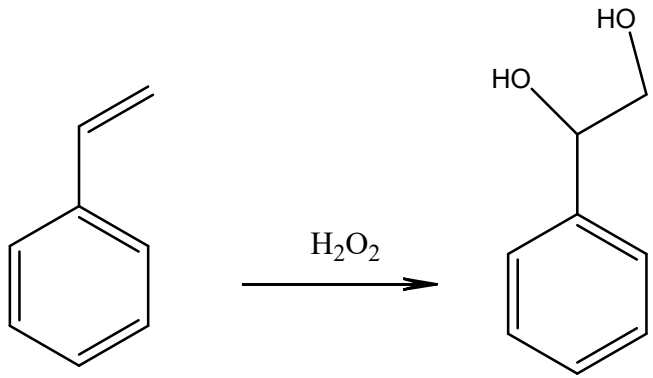
Substrate	Rate constant	Activation energy
Styrene	-0.82128	10.80KJ/mole
Chlorostyrene	-0.80738	5.96KJ/mol
Nitrostyrene	-0.85684	7.53KJ/mole
methylstyrene	-1.09303	5.62KJ/mole
Cyclohexene	-0.84094	11.14KJ/mol

DFT Supporting Data

Table S2

Molecule	Vacuum (E_h)	Solvent (E_h)	Solvation Energy kcal/mol
H_2O_2	-151.5468424	-151.5583898	-7.246034417
H_2O	-76.42256054	-76.43325217	-6.7090299
O	-74.96488477	-74.96728249	-1.504576093
$OH^{\cdot}$	-75.74348112	-75.75046408	-4.381828349
$OOH^{\cdot}$	-150.9198393	-150.9286625	-5.536640945
$H^{\cdot}$	-0.498764285	-0.49888577	-0.076232562

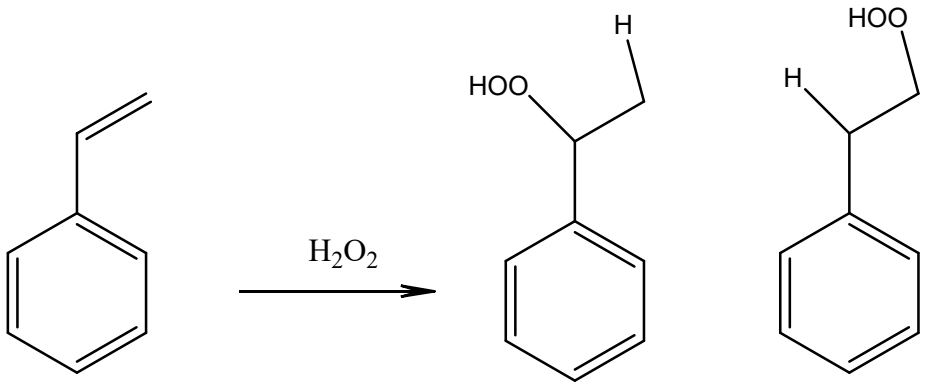
Reaction	ΔG (kcal/mol)
$H_2O_2 \rightarrow H_2O + O$	99.05454969
$H_2O_2 \rightarrow 2OH^{\cdot}$	36.05732638
$H_2O_2 \rightarrow H^{\cdot} + OOH^{\cdot}$	82.10340219



Reaction Scheme 1 (Intermediate 1)

Table S3

Vacuum (E_h)			Solvent (E_h)			ΔG (kcal/mol)
Styrene	**H_2O_2**	**Int 1**	**Styrene**	**H_2O_2**	**Int 1**	
-309.4581374	-151.5468424	-461.0879714	-309.4628591	-151.5583898	-461.1038436	-51.83

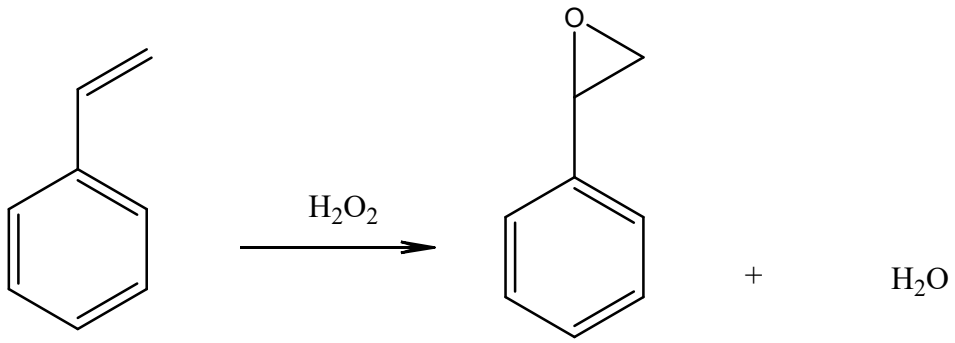


Reaction Scheme 2 (Intermediate 2A or 2B)

Table S4

Vacuum (E_h)			Solvent (E_h)			ΔG (kcal/mol)
Styrene	**H_2O_2**	**Int 2A**	**Styrene**	**H_2O_2**	**Int 2A**	
-309.4581374	-151.5468424	-461.0042952	-309.4628591	-151.5583898	-461.0172822	2.48

Vacuum (E_h)			Solvent (E_h)			ΔG (kcal/mol)
Styrene	**H_2O_2**	**Int 2B**	**Styrene**	**H_2O_2**	**Int 2B**	
-309.4581374	-151.5468424	-461.0028449	-309.4628591	-151.5583898	-461.0155513	3.57



Reaction Scheme 3

Table S5

Molecule	Vacuum (E_h)				Solvent (E_h)			
	Styrene	**H_2O_2**	**Oxide**	**H_2O**	**Styrene**	**H_2O_2**	**Oxide**	**H_2O**
Styrene	-309.4581374	-151.5468424	-384.6521644	-76.42256126	-309.4628591	-151.5583898	-384.6601795	-76.43325676
Chlorostyrene	-769.033453	-151.5468424	-844.227141	-76.42256126	-769.038951	-151.5583898	-844.2356754	-76.43325676
Methylstyrene	-348.7358112	-151.5468424	-423.9296224	-76.42256126	-348.741395	-151.5583898	-423.9383657	-76.43325676
Nitrostyrene	-513.9660216	-151.5468424	-589.1591697	-76.42256126	-513.9773834	-151.5583898	-589.173286	-76.43325676
Cyclohexene	-234.4518534	-151.5468424	-309.650181	-76.42256126	-234.4542727	-151.5583898	-309.6564001	-76.43325676

Molecule	ΔG kcal/mol
Styrene	-45.29
Chlorostyrene	-44.92
Methylstyrene	-45.08
Nitrostyrene	-44.41
Cyclohexene	-48.31

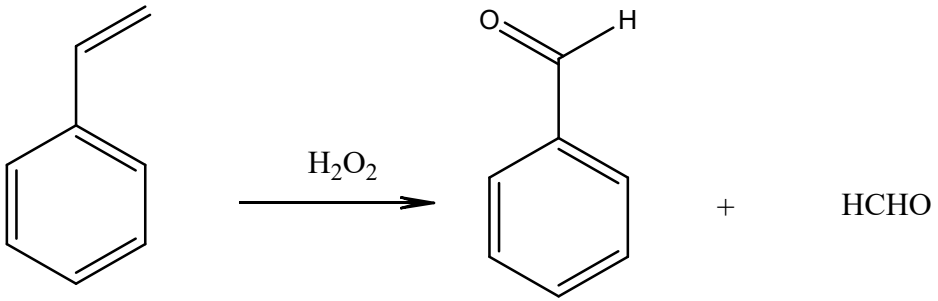
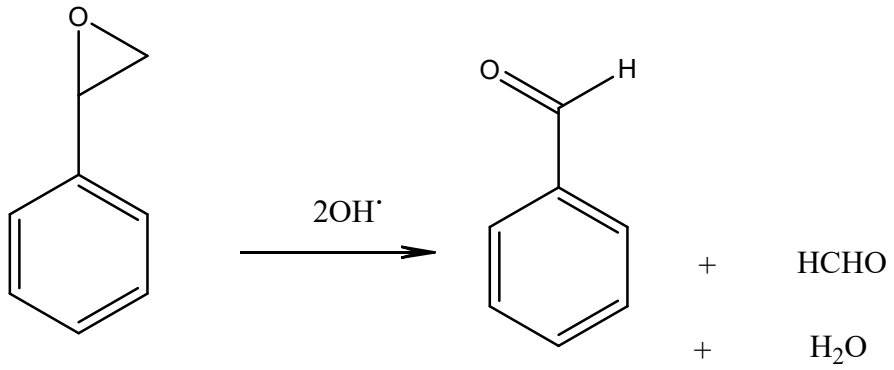


Table S6

Molecule	Vacuum (E_h)				Solvent (E_h)				ΔG kcal/mol
	Styrene	H_2O_2	Aldehyde	Formaldehyde	Styrene	H_2O_2	Aldehyde	Formaldehyde	
Styrene	-309.458137	-151.54684	-345.422430	-114.4895901	-309.46285	-151.55838	-345.432138	-114.4959154	686.98
Chlorostyrene	-769.033453	-151.54684	-804.997263	-114.4895901	-769.03895	-151.55838	-805.007117	-114.4959154	687.68
Methylstyrene	-348.735811	-151.54684	-384.700208	-114.4895901	-348.74139	-151.55838	-384.711674	-114.4959154	685.35
Nitrostyrene	-513.966021	-151.54684	-549.926250	-114.4895901	-513.97738	-151.55838	-549.941277	-114.4959154	689.36



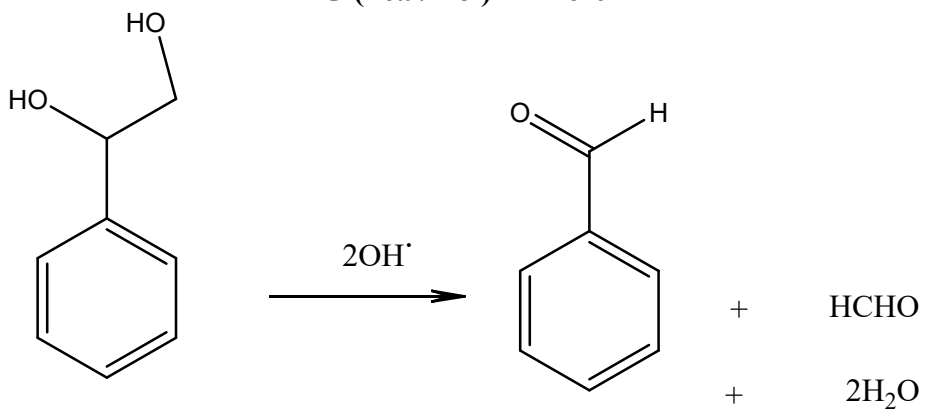
Styrene oxide to Benzaldehyde

Table S7

Vacuum (E_h)				
Oxide	**OH·**	**Aldehyde**	**HCHO**	**H_2O**
-384.6521644	-75.74348112	-345.4224303	-114.4895901	-76.42256054

Solvent (E_h)				
Oxide	**OH·**	**Aldehyde**	**HCHO**	**H_2O**
-384.6601795	-75.75046408	-345.4321381	-114.4959154	-76.43325217

ΔG (kcal/mol) = -125.62



Intermediate 1 to Benzaldehyde

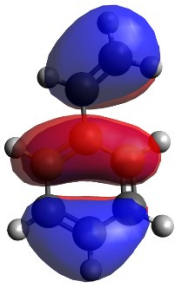
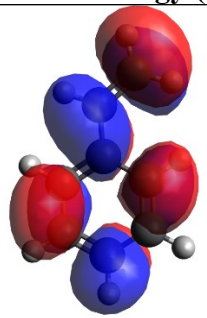
Table S8

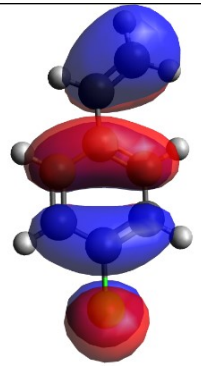
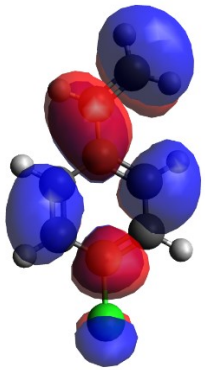
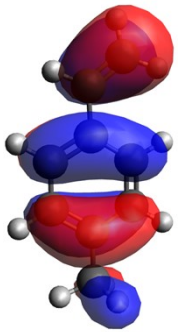
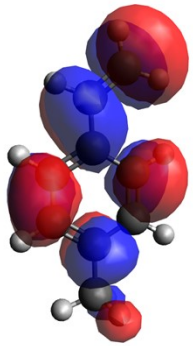
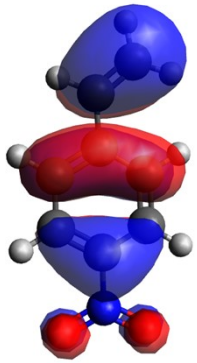
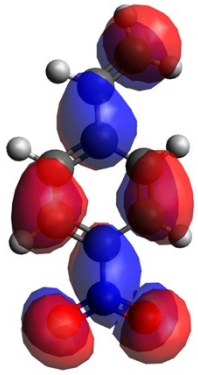
	Vacuum (E_h)				
	Int 1	**OH·**	**Benzaldehyde**	**HCHO**	**H_2O**
	-461.0879714	-75.74348112	-345.4224303	-114.4895901	-76.42256054

Solvent (E_h)				
Int 1	**OH·**	**Benzaldehyde**	**HCHO**	**H_2O**
-461.1038436	-75.75046408	-345.4321381	-114.4959154	-76.43325217

ΔG (kcal/mol) = -119.09

Table S9. Comparative aspect of HOMO and LUMO energies

Molecule	HOMO Orbital energy (eV)	LUMO Orbital energy (eV)	HOMO-LUMO gap (eV)
Styrene	 -6.3222	 -1.2282	5.094

Chlorostyrene	 -6.3013	 -1.3686	4.9327
Methylstyrene	 -6.1244	 -1.1257	4.9987
Nitrostyrene			

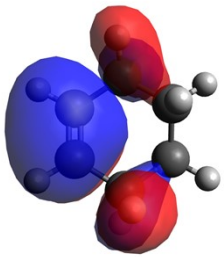
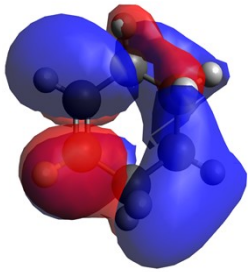
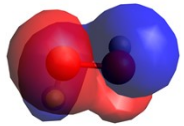
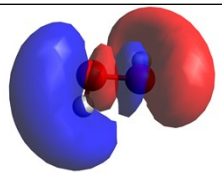
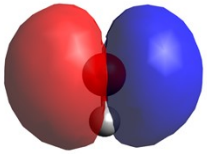
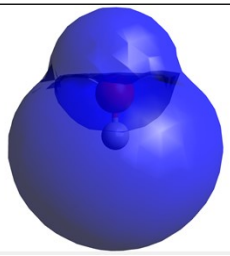
	-6.7953	-2.8828	3.9125
Cyclohexene	 -6.5629	 0.4937	7.0566
H_2O_2	 -8.1644	 0.1942	8.3586
$OH^{\cdot}$	 -9.4555	 1.3251	10.7806

Table S10. Comparison table

Sl. No.	Reactant(s)	Catalyst	Time (hr)	Temperature (°C)	Molar ratio of Oxidant Sty:oxidant	Conversion (%)	Selectivity (%)	Reference
1)	Styrene	MOF	24	100	2mM TBHP	99	70	(1)
2)	Styrene	Au-Ag nanocluster	24	65	1.5mM TBHP	78.9	63.9	(2)
3)	Styrene	Gold nanoparticles supported on dendrimer	24	80		95	50	(3)
4)	Styrene	$CoFe_2O_4$	5	80	1:2 Sty:TBHP	81.8	76.2	(4)
5)	Styrene	Cerium	9	70	2:3	59.4	10.2	(5)

		doped Cobalt ferrite			Sty:H_2O_2			
6)	Styrene	Co-Al_2O_3		90		75.8	56.6	(6)
7)	Styrene	$NiCo_2O_4$	10	70	1:3 Sty:H_2O_2	78	67	(7)
8)	**Our work**	**TiCo(NP)^{HT}**	**6**	**50**	**1:2 Sty:H_2O_2**	**88.3**	**85.1**	**Present work**

References:

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