Supporting Information

Thermal Catalytic Mineralization of ortho Dichloro Benzene at Low Temperature: An *in situ* FT-IR and XPS mechanistic investigation.

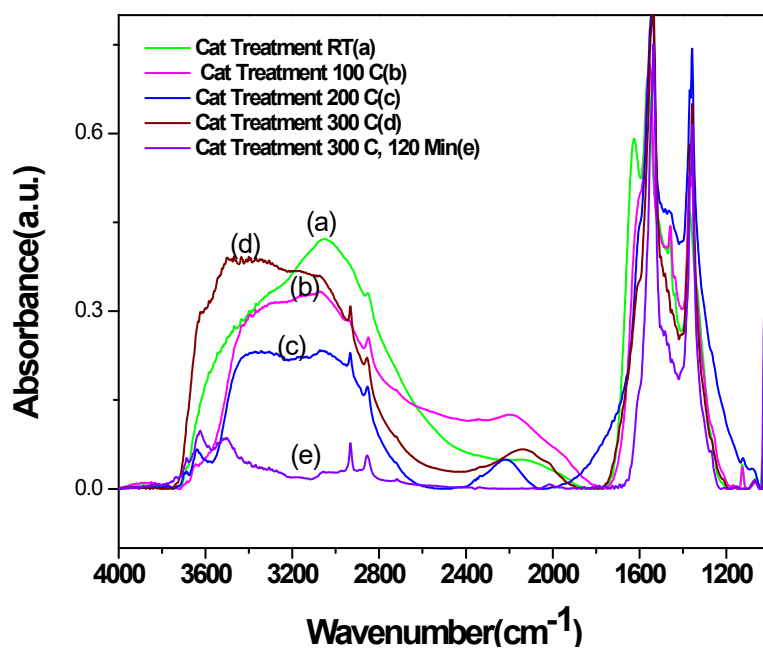Adarsh Kumar[a, b], Deepak Tyagi[a, b], Salil Varma[a, b], Hushan Chand[c], V. Krishnan[c],

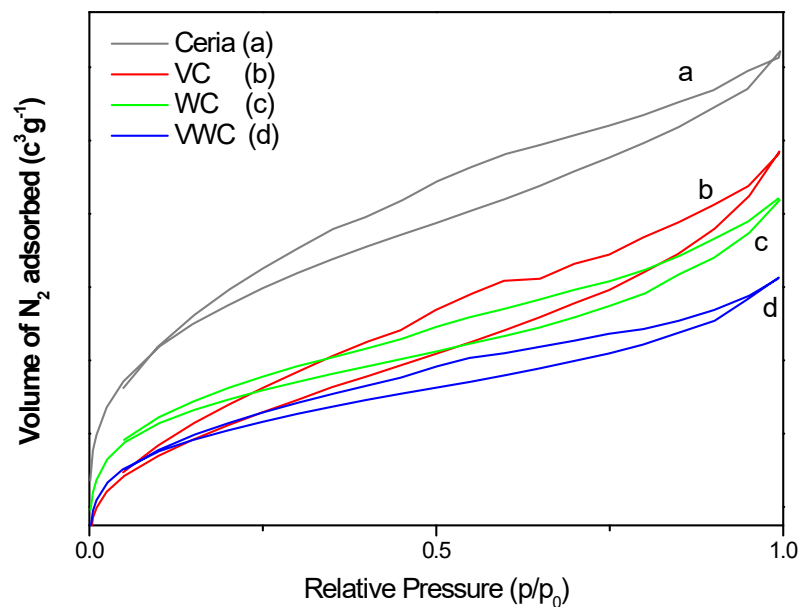K. Bhattacharyya*[a, b], A. K. Tyagi*[a, b].

a- Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400 085, India

b- Homi Bhabha National Institute, Mumbai - 400 094, India
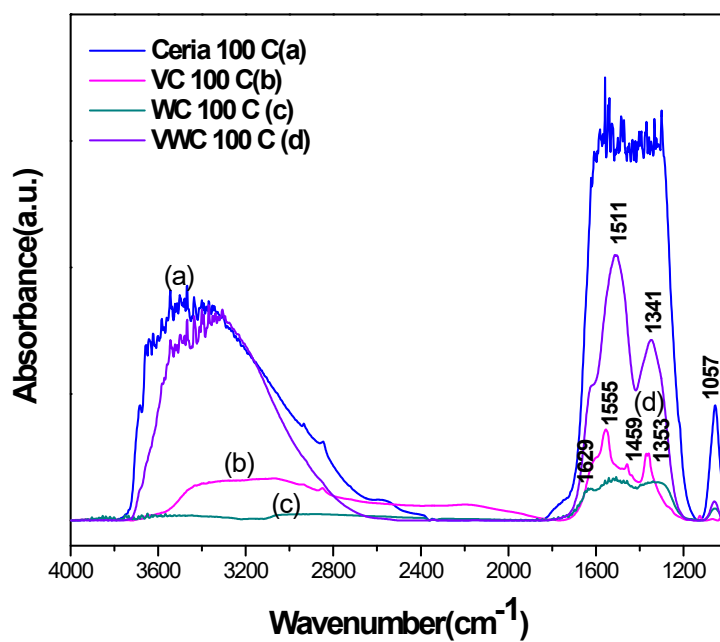
c- Indian Institute of Technology- Mandi, Kamand, Mandi - 175 075, India

.

Fig.S.1 -Catalyst Pre-treatment for VC catalysts at a) Room Temperature (RT); b) 100 °C; c) 200 °C; d) 300 °C; e) 300 °C after 120 min.

Fig.S.2 -Nitrogen adsorption-desorption isotherms of (a) Ceria, (b) VC, (c) WC, (d) VWC.

Fig.S.3 -FT-IR spectra for the different sample (a) Ceria, (b) VC, (c) WC, (d) VWC

| Sample	Ce $3d_{5/2}$					Ce $3d_{3/2}$					Ce^{3+}(%)
Peak assignment	v^o	v	v'	v''	v'''	u^o	u	u'	u''	u'''	
VC	879.7	881.6	884.4	887.8	899.1	897.7	900.1	901.7	905.9	915.9	31
WC	879.8	881.9	884.8	887.9	895.8	897.9	900.3	902.3	906.7	915.9	34
VWC	879.5	881.6	884.8	887.9	896.9	897.8	900.1	902.8	906.5	915.9	31
VC-used	879.9	881.9	884.6	887.9	895.9	898.1	900.5	902.9	906.7	915.9	46
WC-used	879.8	881.6	884.5	887.9	895.9	897.8	900.1	902.5	906.9	915.9	46
VWC-used	879.5	881.9	884.9	888.5	895.9	895.7	900.6	902.8	906.9	915.9	53

Table: S-1. Concentration of the Ce^{3+} present in the different Samples and the samples after being used as a Catalyst.

Sl No.	Sample	Element	Position (eV)	FWHM	Atom (%)
1	V_2O_5-CeO_2 (VC)	O-1s	529.47	3.24	87.22
		Ce-3d	881.47	7.18	10.98
		V-2p	516.47	2.18	1.80
2	WO_3-CeO_2 (WC)	O-1s	529.40	3.03	82.26
		Ce-3d	881.48	7.37	12.52
		W-4d	247.48	5.03	5.23
3	V_2O_5-WO_3-CeO_2 (VWC)	O-1s	529.47	2.78	82.19
		Ce-3d	881.47	7.01	11.76
		W-4d	247.48	4.829	2.57
		V-2p	516.47	2.309	3.48

Table: S-2. Concentration of the Catalyst on Surface Elemental Concentration from XPS

Sample	O-1sXPS- (O-Vacancy)	O-1sXPS- (O-Vacancy) (%)	O-1sXPS- (O-Vacancy) -Used Sample(%)	O-1sXPS- (O-Vacancy) -Used Sample(%)
VC	533.3	7.4	532.4	6.3
WC	532.33	5.8	532.72	3.72
VWC	532.5	3.6	533.03	3.3

Table: S-3. Concentration of the O-vacancy after the reaction the different Thermal

Catalyst from XPS
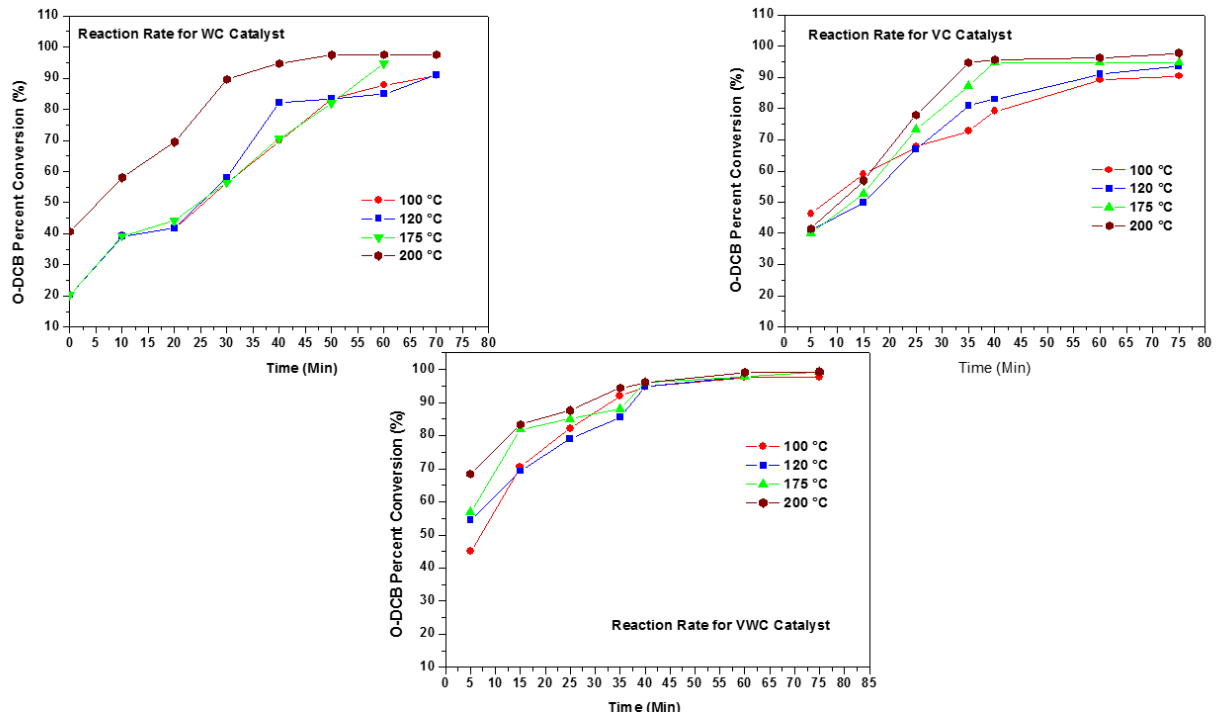
Fig.S.4. -Kinetics for the percent conversion of o-DCB (%) as CO_2 as a product for oxidation of o-DCB using different Catalyst showing the Percent o-DCB conversion the three Different Catalysts A) VC; B) WC and C) VWC as a function of temperature for: 1) 100 °C; 2) 120 °C; 3) 175 °C; 4) 200 °C.

Percent Conversion (%) = $\dfrac{VCO2(ml)}{ACO2(ml)}$ x100………………. (1)

Where V_{CO2} = Volume of CO_2 produced as calculated from the FT-IR using Calibration Curve

A_{CO2} = Stoichiometric total amount of CO_2 to be produced by complete oxidation of o- DCB using the equation -2

$$C_6H_4Cl_2 + 7O_2 \xrightarrow[\text{Temperature}]{\text{Catalyst}} 6CO_2 + 2HCl + 2H_2O \quad \ldots\ldots\ldots (2)$$
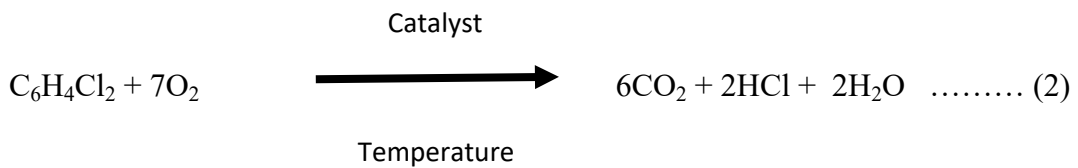
Volume of CO_2 to be produced Stoichimetrically = 6 x Volume of *o*-DCB in the static reactor

Volume of O-DCB present = Volume of o-DCB taken X 600 ppm x 3
$$= 50 \times 600 \times 10^{-6} \text{ cc} \times 3$$
$$= 9 \times 10^{-2} \text{ cc}$$
Therefore, total amount of CO_2 produced by complete oxidation of o-DCB= 0.09x6 = 0.54 cc
$$= A_{CO2}$$

6

Sl. No.	Catalyst	Catalytic Reaction studied @ T(°C)	Final Desorption Temperature in Oxygen atmosphere (°C)	Final Desorption Temperature in He atmosphere (°C)
1	VC	100	200	200
		120	200	200
		175	200	-
		200	225	-
2	WC	100	225	300
		120	220	300
		175	300	-
		200	300	-
3	VWC	100	300	300
		120	250	300
		175	300	-
		200	300	-

Table: S-4. Typical Desorption temperature for the catalytic reaction of O-DCB and air and without oxygen.

| 1/2r	1/r	R(nm)	D(Å)	JCPDS (77-2418)	Plane
134.084	67.042	0.014916	1.491602	1.4932	(7 1 0)
151.012	75.506	0.013244	1.324398	1.3362	(6 1 2)
215.012	107.506	0.009302	0.930181	1.1029	(6 1 3)
252.991	126.4955	0.007905	0.790542		
300.005	150.0025	0.006667	0.666656		

Table: S-5. (A) SAED pattern calculation for the sample - VC

1/2r	1/r	R(nm)	D(Å)	JCPDS (83-0950) WO3-Cubic JPCS 56, 1995,1305.	Plane
129.955	64.9775	0.01539	1.538994	1.5029	(4 2 2)
150.087	75.0435	0.013326	1.33256	1.3338	(4 0 4)
212.989	106.4945	0.00939	0.939016	1.1029 V2O5 (77-2818)	(6 1 3)
246.067	123.0335	0.008128	0.812787		
317.998	158.999	0.006289	0.628935		

**Table: S-5**. (B) SAED pattern calculation for the sample - VWC.
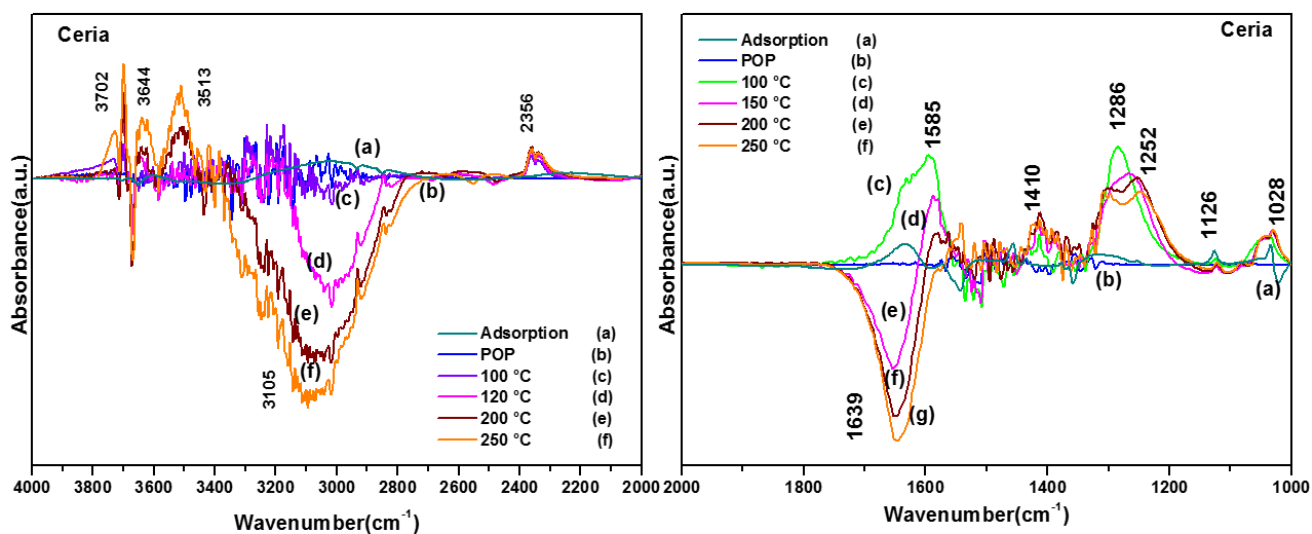
Fig.S-5: Adsorption and Reaction of o-DCB and air mixture (40 cc) with Ceria Support as a function of temperature: a) Adsorption; b) Pellet on Pellet; c) 100 °C, d) 120 °C; e) 200 °C; f) 250 °C. The panel A shows the vibrational bands from (4000-2000) cm^{-1} and the panel B shows the vibrational bands from (2100-1000) cm^{-1}.

The adsorption of o-DCB and air on ceria leads to different vibrational bands at (3609, 3038, 1633, 1456, 1316, 1127, 1033) cm^{-1} with two negative peaks at (1542 and 1356) cm^{-1}. The peak at 3609 cm^{-1}, is mostly the surface -OH group present in the ceria itself and the 3038 cm^{-1} should be the bond formed by the surface -OH formed after adsorption of the enolate species over the surface. 1633 cm^{-1} (represents enolates); 1456 cm^{-1} (represents π-ring complex); (1316 & 1127) cm^{-1} (represent phenolates); 1033 cm^{-1} (chloro sensitive phenolate)[3]; The negative bands are the -OH bands of the Ceria itself which it utilizes to form phenolate or enolate. Therefore, o-DCB and air upon adsorption follows the Scheme-1 of adsorption along with formation additional π-ring complex. The vibrational bands obtained at 100 °C are 3515 cm^{-1} (Surface -OH); 3013 cm^{-1} (the surface -OH produced by enols -used so showing negative band) ; 1588 & 1282 cm^{-1} (assigned for enolates); 1415 cm^{-1} (represents maleate) as presented in Table-3. At 120 °C the negative peak at 3013 cm^{-1} increases in intensity with other new negative peak at 1652 cm^{-1} (representing used surface enolates mostly); a small peak with low intensity at 1586 cm^{-1} (enolate formed) 1269 cm^{-1} (acetates formed); with a small amount of gaseous CO2 (2362, 2328 cm^{-1}) formed. This represent a dynamic scenario where some enolates are used to form acetates and CO_2 and some more enolates are formed. At higher

temperature of 200 and 250 °C there are low intensity (as compared to the VC/WC/VWC) peaks at (3644, 3513, 2363, 2328) cm^{-1} (showing formation of gaseous CO_2) negative peak at 1650 and 3105 cm^{-1} (increasing as a function of temperature), and lowering intensity peak at 1583 cm^{-1}. A new peak is observed at 1546 cm-1 (250 °C) [representing acetates] and at 1256 and 1245 cm^{-1} (also representing acetates). Therefore, in the support though there is formation of some gaseous CO_2 it is very less as compared to VC/WC /VWC catalysts and mainly through acetate as an intermediate. [All the intermediates are taken from the Table -3 and accordingly the References can be utilised also]

TG-DSC -studies for the Ce(III) carbonate to show formation of CeO$_2$

TG-DSC studies for decomposition of cerium (III) carbonate were carried out under flowing air for delineation of optimum temperature for synthesis of ceria. As shown in Fig. 1.2, cerium (III) carbonate undergoes decomposition in two steps, first step for 80-150°C temperature range corresponding to moisture loss, followed by second step for 200-300 °C temperature range for loss of carbon dioxide resulting residue of CeO_2.
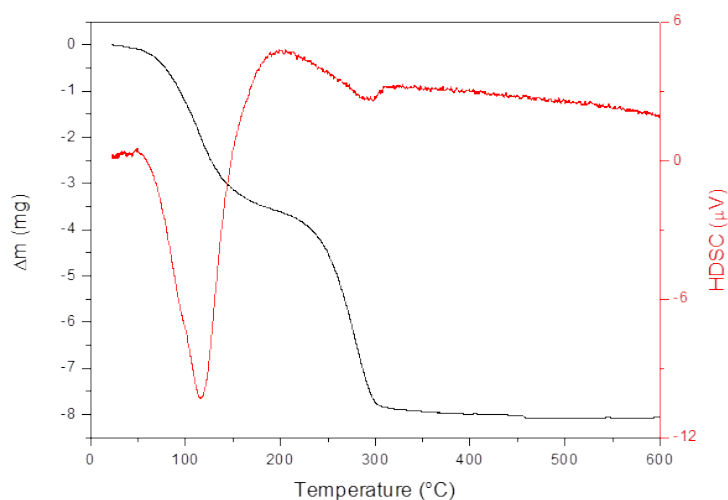
Fig.S-6 : TG-DSC for decomposition of Cerium (III) carbonate under air flow

Synthesis and characterization of nano CeO$_2$.

Based on TG-DSC measurements, cerium oxide (CeO_2) has been prepared by heating cerous carbonate at 250 °C and 350 °C. Both samples resulted in single phase ceria matching to JCPDS No. 34-0394 corresponding to cubic symmetry, with crystallite size of ~ 6nm as shown in Fig. S.7.
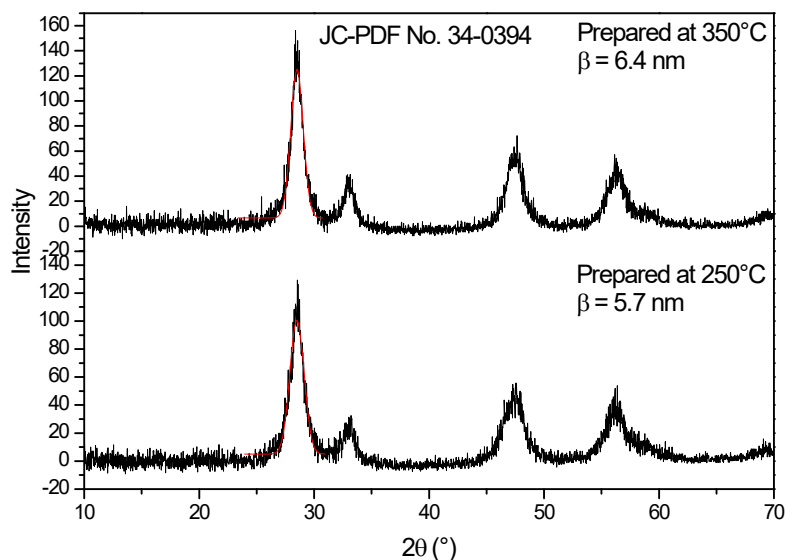
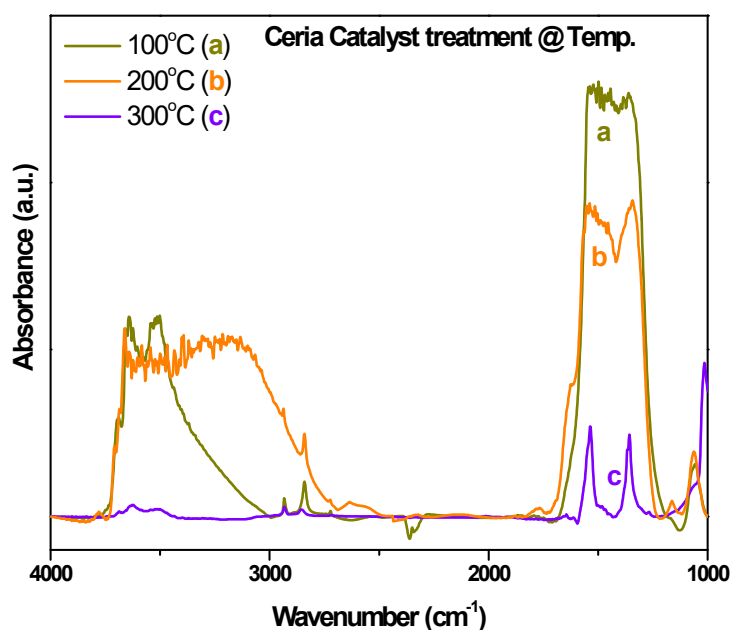Fig. **S-7**: XRD patterns for Ceria prepared by direct decomposition of cerous carbonate at 250 and 350 °C.

Fig.S-8: FT-IR data for the CeO_2 catalysts as a function of Temperature: a) 100 °C; b) 200 °C; c) 300 °C.

Also it can be understood from the Fig.S-8 below that as a function of temperature these bands gets reduced in intensity which clearly shows that they are of surface -OH or H_2O which gets reduced as a function of temperature. The above Fig.3 depicts *in situ* calcination of the CeO_2 pellet as a function of temperature and it is quite evident that the intensity of these bands at 1600-1300 cm^{-1}(in question) are reduced as function of temperature. This clearly proves that

they belong to surface -OH or surface H_2O which gets reduced as a function of temperature and are not exactly bands for CeO_2. At around 200 °C similarly bands at (1630 and 1380) cm^{-1} are due to that of H-OH bend over the ceria surface (Fig.3.b). Same has been already observed by Vargehse *et al.* (Indian Journal of Pure & Applied Physics 53, **2015**, 596-603) for the as synthesised CeO_2, Karuthapandian *et al.* (Optik 154, **2018**, 242–250) etc. in the previous literature. However, at 300 °C (Fig.3.c) it is quite evident that the bands at (1529 and 1350) cm^{-1} as is observed for CeO_2 which are mostly identical characterization FT-IR data of CeO_2 in earlier reports [Bulletin UASVM Food Science and Technology 72(1), 2015 and M. Panahi-Kalamuei et al. Journal of Industrial and Engineering Chemistry 21, 2015, 1301–1305]. this clearly shows that the CeO_2 was synthesised purely observed in the region 1300-1600 cm^{-1} were for the surface -OH group which will always be present with any mixed oxide. The above part is also appended in the Supporting information as Fig. S-8. All the Figures are appended here for the ready reference of the reviewer.