Supporting information

XPS figure of Au/Ca-CeO2 maintaining same FWHM

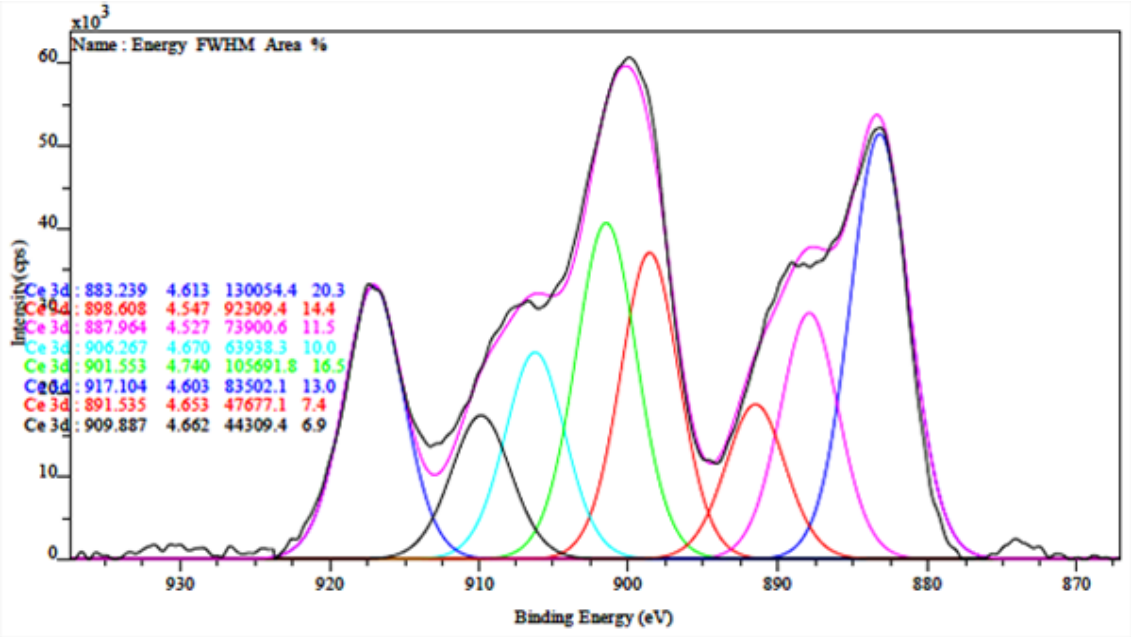

Fig. 1: Ce (3d) core level XPS spectra.

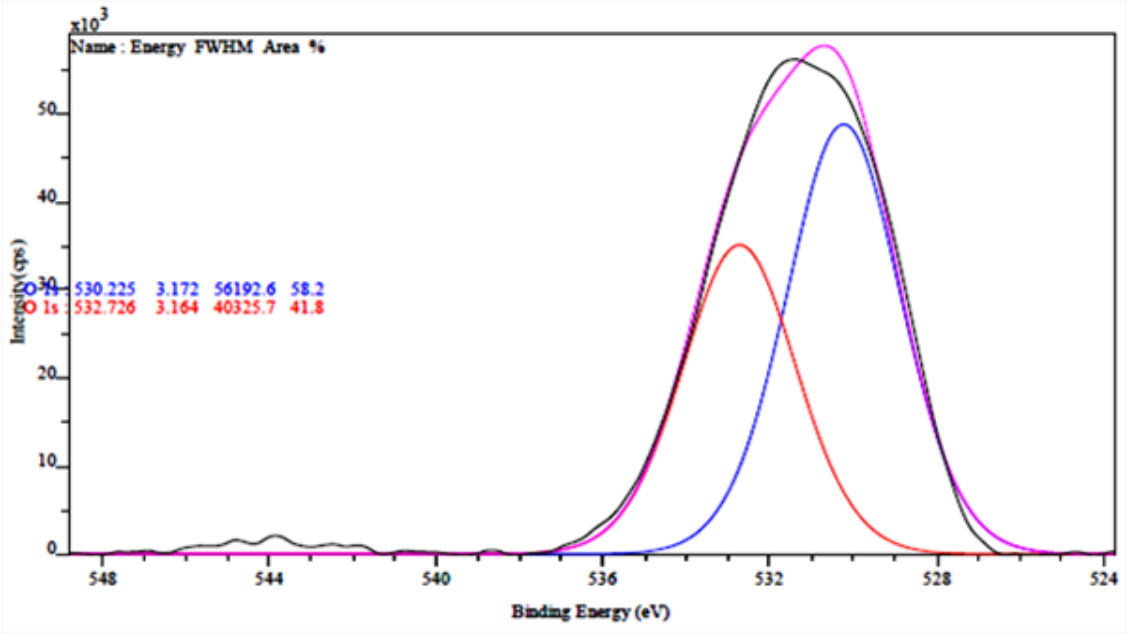

Fig. 2: O (1s) core level XPS spectra.

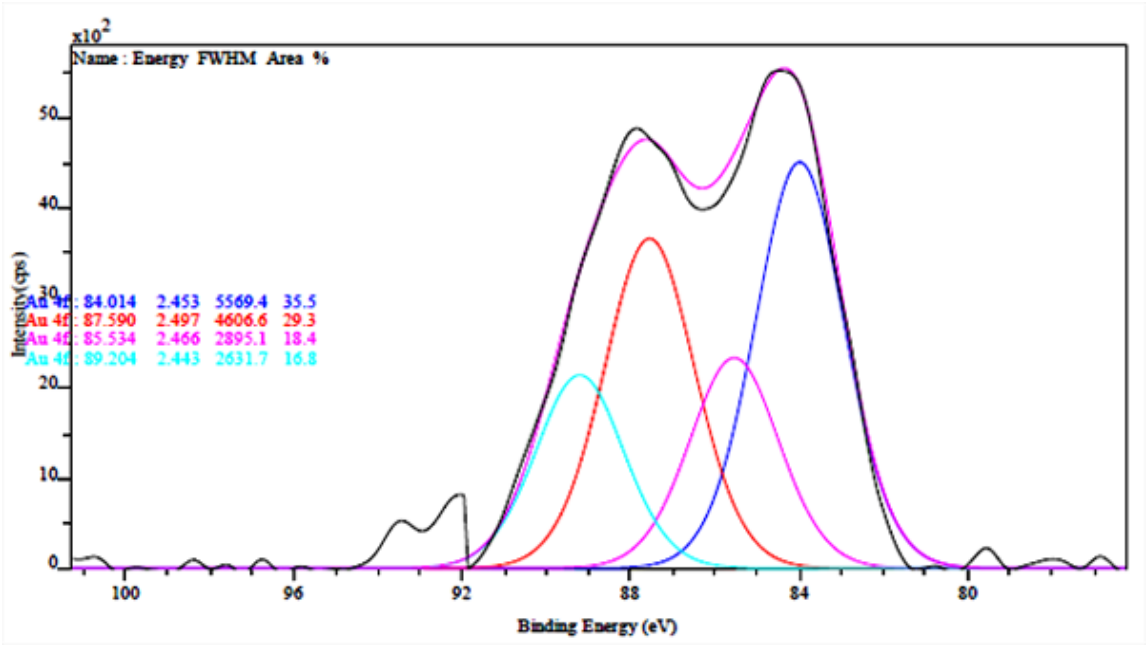

Fig. 3: Au (4f) core level XPS spectra.

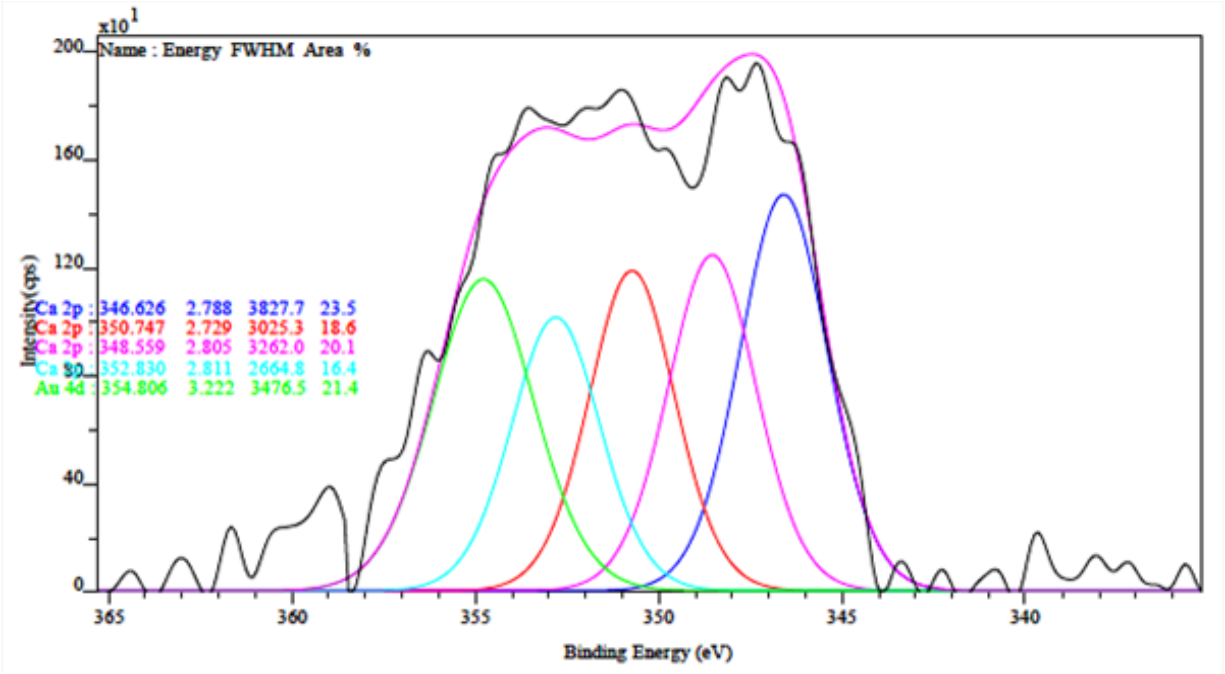

Fig. 4: Ca (2p) core level XPS spectra.

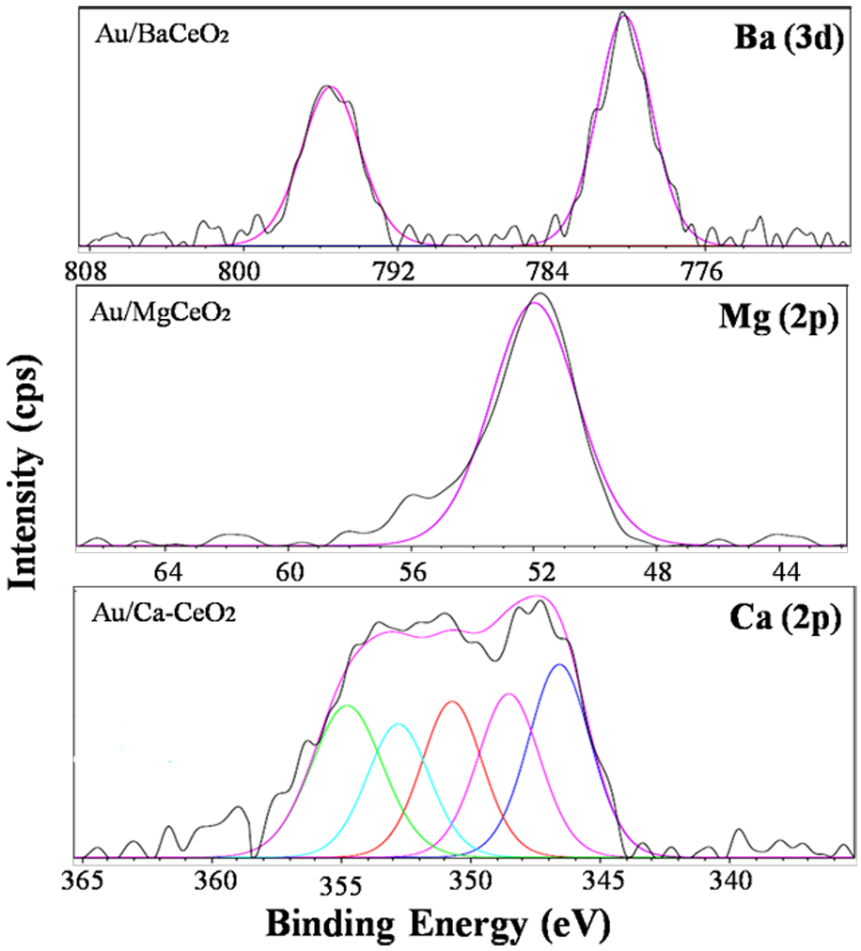

Fig. 5: Mg (2p), Ca (2p) and Ba (3d) core level XPS spectra.

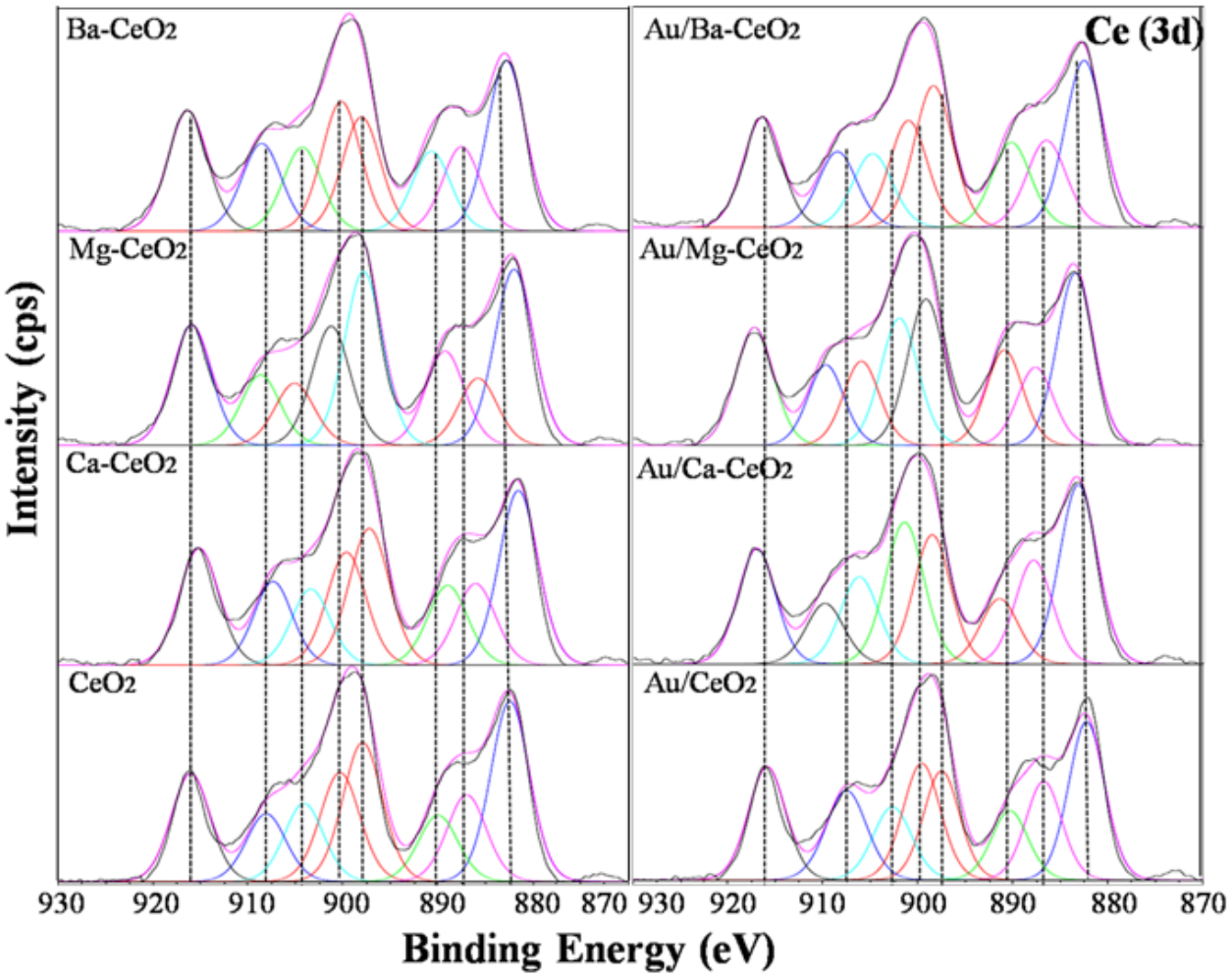

Fig. 6: Ce (3d) core level XPS spectra.

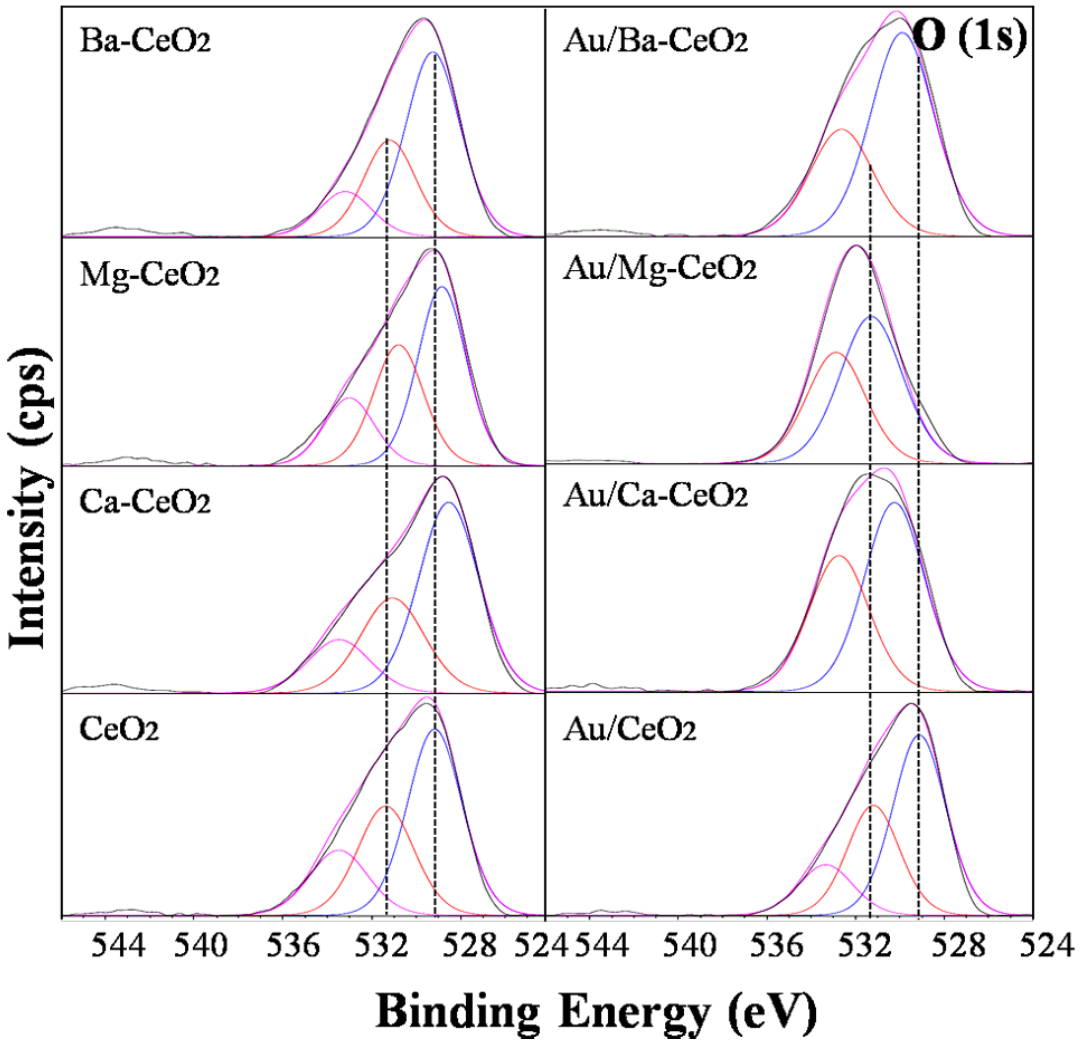

Fig. 7: O (1s) core level XPS spectra.

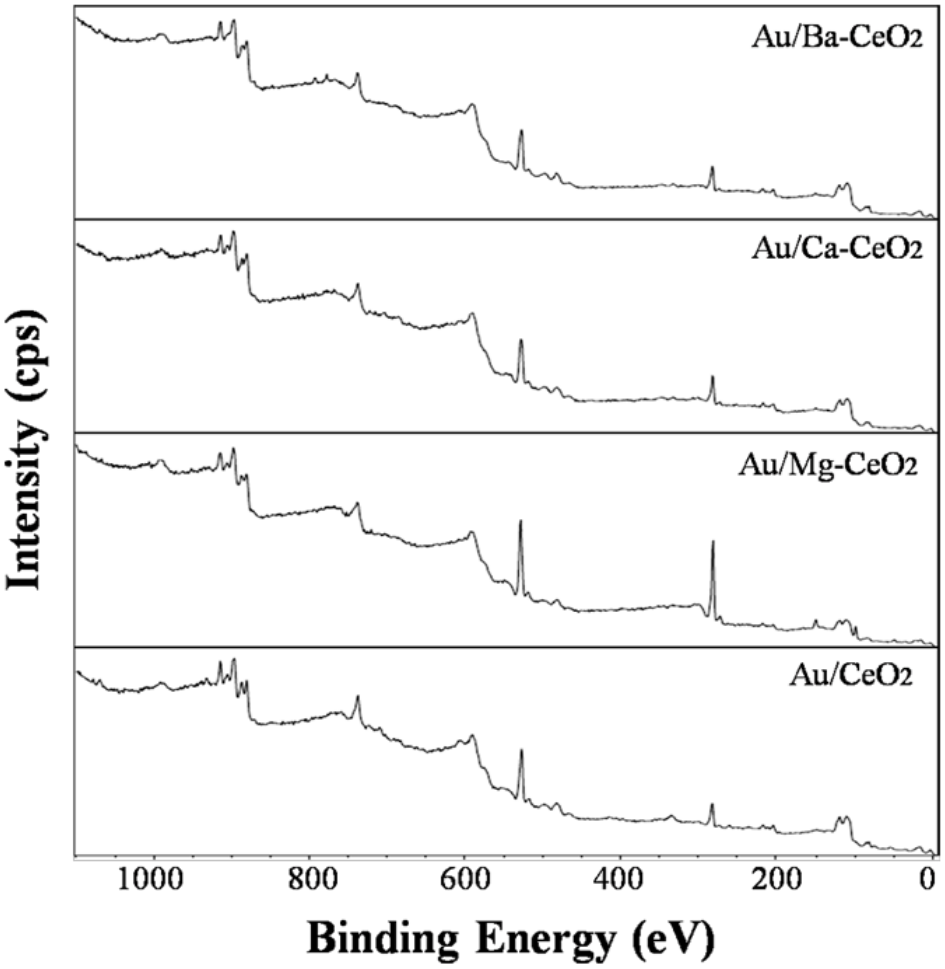

Fig. 8: XPS survey of 2.33 Wt. % of Au on Ba-CeO_2 (Ba/Ce =4/100), Ca-CeO_2 (Ca/Ce =4/100), Mg-CeO_2 (Mg/Ce =4/100) and CeO_2

Calculation of TOF of Au/Ba-CeO_2

Taking 4mmol of Benzyl alcohol as starting reactant and considering its area % is 100.

Now, from the G.C calcultation after the reaction , Benzyl alcohol conversion is 36.8 %.

So, 100 % is 4 mmol, hence 36.8 % is 36.8 X 4 X 10^{-3} /100 moles.

From ICP result we get gold loading is 0.03 wt% (2.33 wt% Au/Ba-CeO2)

Now, 100 g support contained Au is 0.03 g

0.1 g " " " " 0.03 X 0.1 /100 g = 3 X 10^{-5} g

Now, 196.97 g Au is 1 mol

3 X 10^{-5} g Au is 3 X10^{-5}/196.97 g = 1.523 X10^{-7} mol

$$TOF = \frac{\text{No. of moles of PhCH2OH converted}}{\text{No. of moles of Au X Reaction time}}$$

$$= \frac{36.8/100 \text{ X } 4 \text{ X } 10\text{-}3}{1.523 \text{ X } 10\text{-}7 \text{ X } 3}$$

$$= \frac{36.8 \text{ X } 4 \text{ X}10\text{-}3}{100 \text{ X } 1.523 \text{ X } 10\text{-}7 \text{ X } 3}$$

$$= \frac{36.8 \text{ X } 4 \text{ X } 100}{1.523 \text{ X } 3}$$

$$= \frac{147.2 \text{ X } 100}{4.569}$$

$$= 3221.7 \text{ h-1}$$

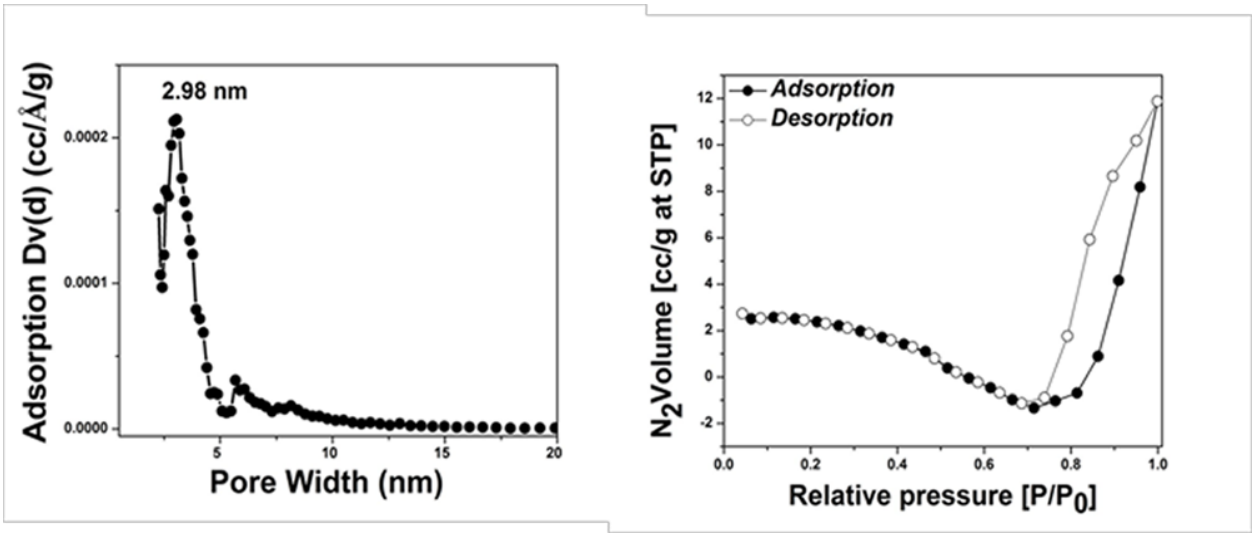

Fig. 9: BET S. A and porosity result of Mg-CeO_2

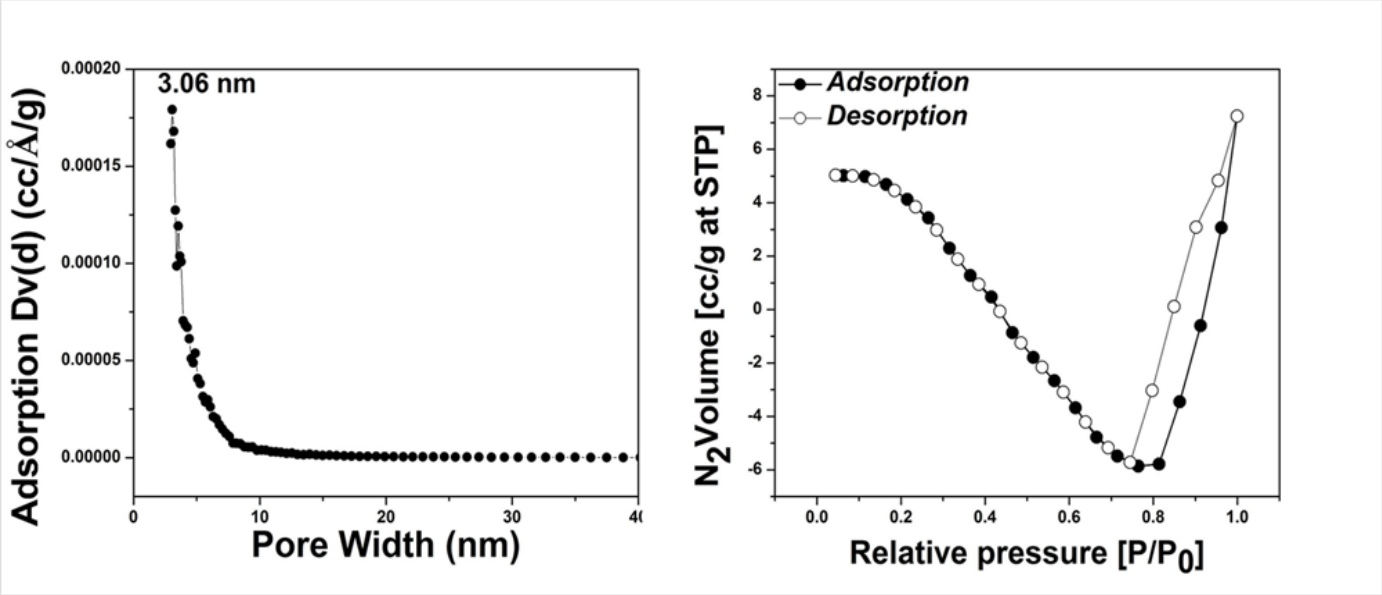

Fig. 10: BET S.A and porosity result of Ba-CeO_2

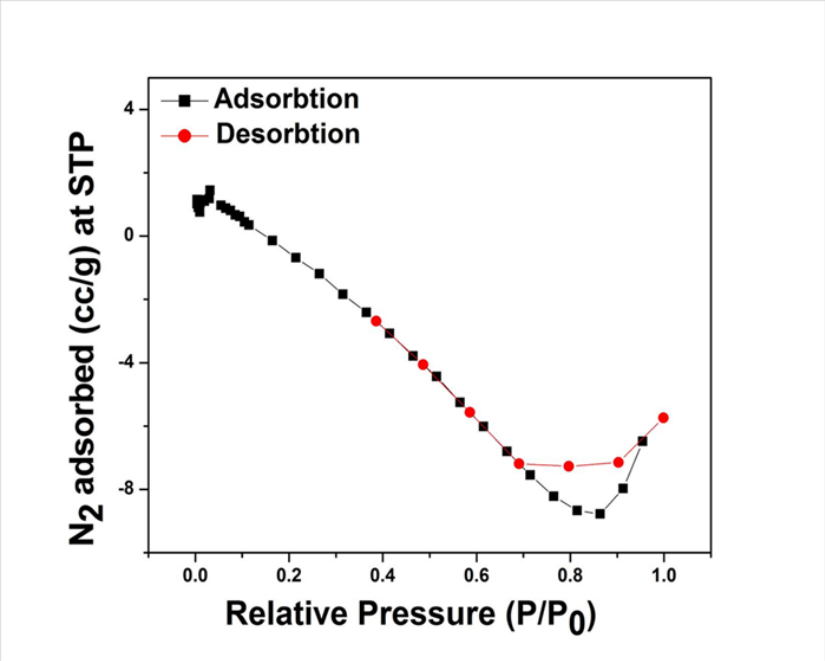

Fig. 11: BET Surface area of CeO_2

Table 1. Quantitative XPS analysis

Catalyst	Ionicity		Covalency			
	Position	Area	Position	Area	Total Area	% Ionic Contribution
CeO_2	529.2	69632.1	531.4	42233.4	111865.5	62.2
$CaCeO_2$	528.1	45535.1	530.4	24195.8	69730.9	65.3
$MgCeO_2$	528.8	52944.2	530.8	37006.6	89950.8	58.8
$BaCeO_2$	529.3	64614.7	531.2	32339.9	96954.6	66.6
Au/CeO_2	529.1	66751.9	531.2	40154.6	106906.5	62.4
$Au/CaCeO_2$	530.2	56192.6	532.7	40325.7	96518.3	58.2
$Au/MgCeO_2$	531.3	73608.1	532.9	52557.0	126165.1	58.3
$Au/BaCeO_2$	529.9	77046.9	532.6	40552.7	117599.6	65.5

Table 2. Result of catalytic activity of 3.5 wt % gold loading in three different support towards benzyl alcohol oxidation.

Catalyst	Gold loading (wt %)	Calcination temperature (^oC)	Conversion (%)	Selectivity (%)
$Au/Mg\text{-}CeO_2$	3.5	300	20.00	> 99
$Au/Ca\text{-}CeO_2$	3.5	300	27.04	> 99
$Au/Ba\text{-}CeO_2$	3.5	300	42.20	> 99

Table 3. Result of catalytic activity of $Au/Ba\text{-}CeO_2$(4 mol% Ba) with different gold loading towards benzyl alcohol oxidation.

Catalyst	Gold loading (wt %)	Calcination temperature (^oC)	Conversion (%)	Selectivity (%)
$Au/Ba\text{-}CeO_2$	1.0	300	27.58	> 99
$Au/Ba\text{-}CeO_2$	2.33	300	36.80	> 99
$Au/Ba\text{-}CeO_2$	3.5	300	42.20	> 99
$Au/Ba\text{-}CeO_2$	4.0	300	22.53	> 99

Table 4. Result of catalytic activity of Au/Ba-CeO_2(4 mol% Ba) with different calcinations temperature towards benzyl alcohol oxidation.

Catalyst	Gold loading (wt %)	Calcination temperature (^oC)	Conversion (%)	Selectivity (%)
Au/Ba-CeO_2	3.5	300	42.20	> 99
Au/Ba-CeO_2	3.5	400	27.56	> 99
Au/Ba-CeO_2	3.5	500	21.76	> 99

Table 5. Result of catalytic activity of Au/Ba-CeO_2(4 mol% Ba) prepared by using different reducing agent towards benzyl alcohol oxidation.

Catalyst	Gold loading (wt %)	Reducing agent	Conversion (%)	Selectivity (%)
Au/Ba-CeO_2	3.5	NaOH	42.20	> 99
Au/Ba-CeO_2	3.5	$NaHCO_3$	38.36	> 99
Au/Ba-CeO_2	3.5	Urea	11.52	> 99

Table 6. Result of catalytic activity of Au/Ba-CeO_2(4 mol% Ba) prepared by using different volume of water taken during HDP method towards benzyl alcohol oxidation.

Catalyst	Gold loading (wt %)	Volume of water (ml)	Conversion (%)	Selectivity (%)
Au/Ba-CeO_2	3.5	50	25.57	> 99
Au/Ba-CeO_2	3.5	100	32.24	> 99
Au/Ba-CeO_2	3.5	150	42.20	> 99

Table 7. XPS quantitative analysis

Catalyst	Position	Area(%)	Position	Area(%)	Position	Area(%)	Position	Area(%)	Ce^{+3}/Ce^{+4}
Ce 3d(5/2)	V		V'		V''		V'''		
Ce 3d(3/2)	U		U'		U''		U'''		
CeO_2	882.4	21.2	887.0	10.4	890.0	8.0	897.9	16.7	0.3273
	900.4	13.2	904.1	9.3	908.1	8.2	916.1	12.8	
$CaCeO_2$	881.5	20.0	886.1	9.6	889.0	9.4	889.6	13.0	0.2880
	903.4	8.7	903.4	8.7	907.4	9.5	915.2	13.6	
$MgCeO_2$	882.1	20.1	885.9	7.6	889.4	10.7	898.0	19.3	0.2087
	901.4	13.4	905.3	7.2	908.9	8.1	916.1	13.7	
$BaCeO_2$	882.7	19.2	887.6	9.5	890.8	9.1	898.2	13.1	0.2449
	900.2	15.0	904.4	9.6	908.7	10.4	916.5	14.1	
Au/CeO_2	882.3	18.5	886.8	11.6	890.3	8.2	899.7	14.2	0.3550
	890.3	8.2	902.7	9.2	907.6	11.8	915.8	13.7	
$Au/CaCeO_2$	883.2	20.3	887.9	11.5	901.5	16.5	898.6	14.4	0.3768
	901.5	16.5	906.3	10.0	909.9	6.9	917.1	13.0	
$Au/MgCeO_2$	883.4	18.9	887.7	8.6	901.9	14.4	899.1	16.3	0.2749
	901.9	14.4	905.9	9.2	909.7	8.7	917.2	13.4	
$Au/BaCeO_2$	882.6	19.5	886.6	10.5	890.2	10.1	898.5	16.6	0.3180
	901.1	12.4	904.9	8.9	908.6	9.0	916.4	12.9	

Table 8. Conc. of PhCHO vs. Area (%) of FID.

Conc. of PhCHO (M) in DMF	Area % (FID)
0.026	0.520
0.050	1.133
0.251	7.014
0.501	13.743
1.004	25.967
1.258	31.572
1.502	35.004
2.000	43.383
2.506	49.624
3.012	54.363

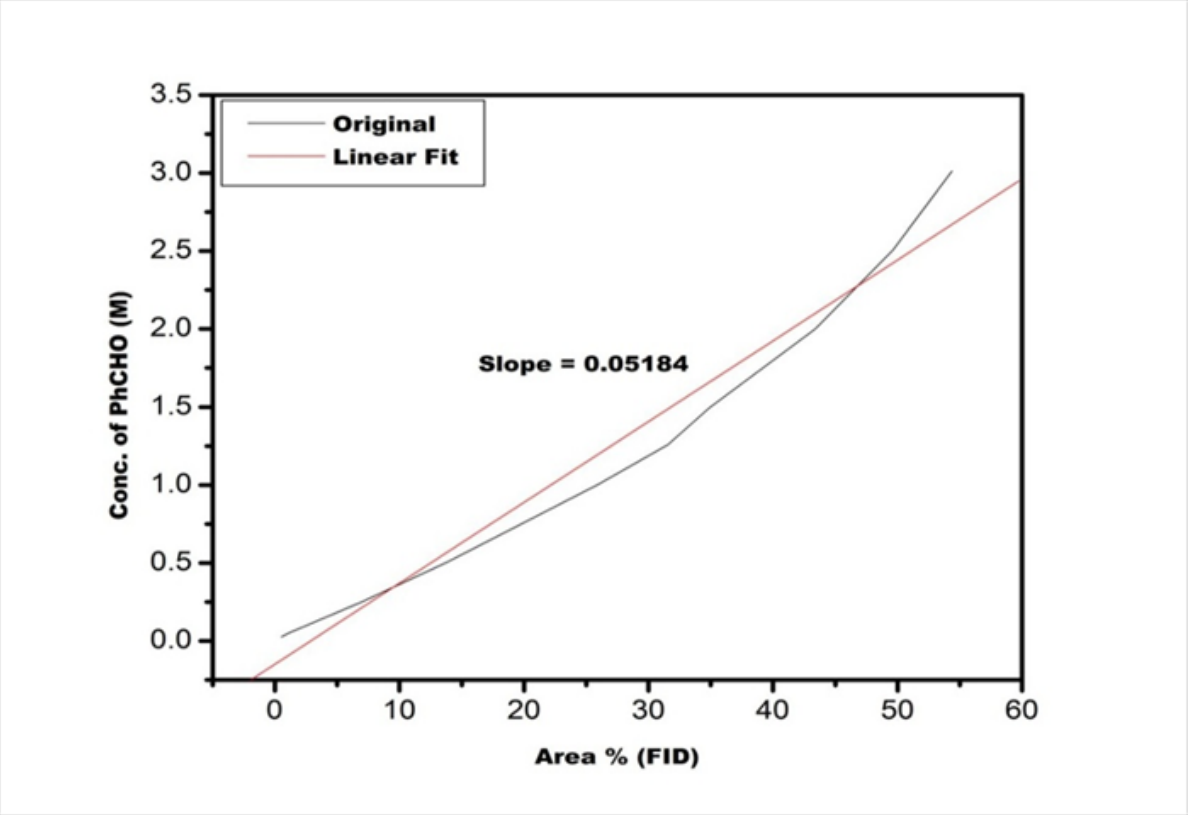

Fig. 12: PhCHO Calibration

Table 9. Conc. of $PhCH_2OH$ vs. Area (%) of FID.

Conc. of $PhCH_2OH$(M) in DMF	Area % (FID)
0.051	0.362
0.254	3.873
0.501	9.557
1.007	20.346
1.251	25.190
1.502	29.884
2.003	37.211
2.502	44.801
3.001	49.538

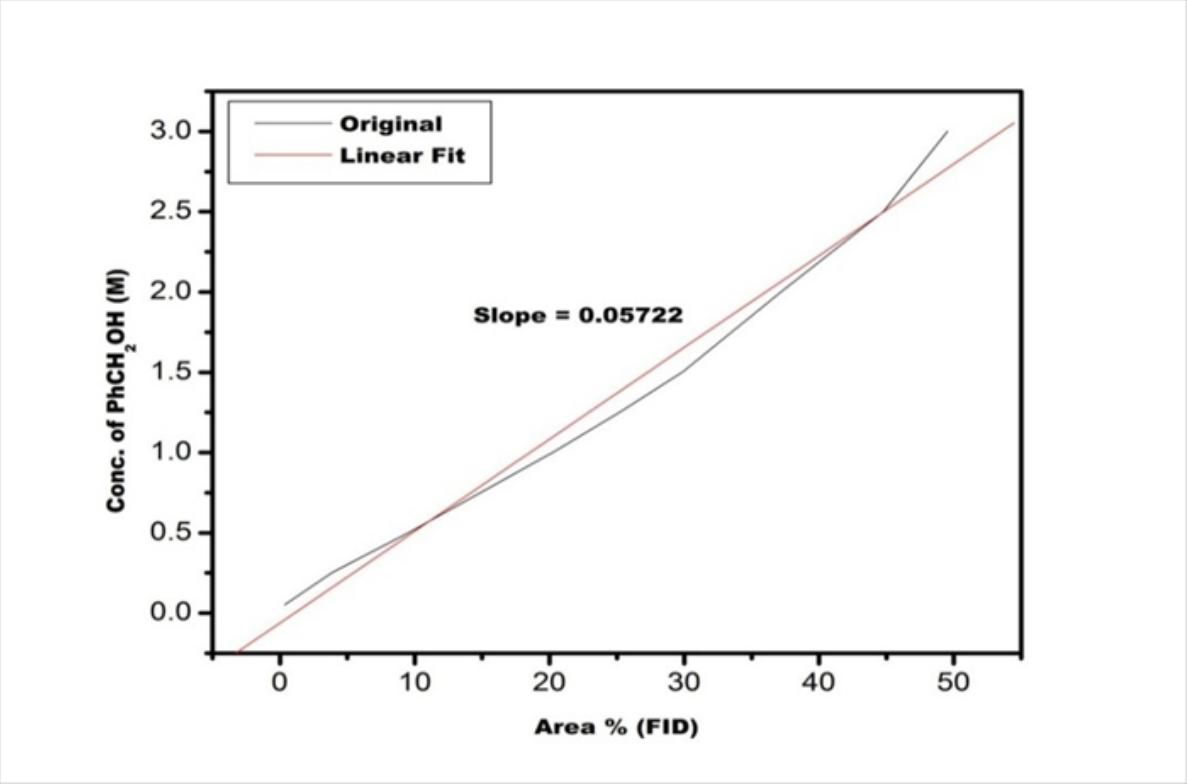

Fig. 13: $PhCH_2OH$ Calibration

Table 10. G.C. Calculation

Calibration Factor (C.F.) of $PhCH_2OH$ =1/0.05722

Calibration Factor (C.F.) of PhCHO =1/0.05184

Area % of $PhCH_2OH$ (Before Reaction) =100

Moles of $PhCH_2OH$(Before Reaction)=100/C.F.
=5.722

After Reaction

Catalyst	Gold Loading wt.%	Area % of $PhCH_2OH$	Moles of $PhCH_2OH$	Area % of PhCHO	Moles of PhCHO	Total Moles	% Mass Balance
CeO2	_	97.370	5.571	2.630	0.136	5.707	99.70
Mg-CeO2	_	97.911	5.602	2.089	0.108	5.710	99.76
Ca-CeO2	_	98.701	5.647	1.299	0.067	5.714	99.85
Ba-CeO2	_	96.131	5.500	3.869	0.200	5.700	99.57
Au/CeO2	2.33	93.889	5.372	6.111	0.316	5.688	99.32
Au/Mg-CeO2	2.33	88.055	5.038	11.945	0.619	5.657	98.67
Au/Ca-CeO2	2.33	79.815	4.567	20.185	1.046	5.613	97.76
Au/Ba-CeO2	2.33	67.000	3.833	33.000	1.710	5.543	96.33
Au/Mg-CeO2	3.50	79.601	4.554	20.399	1.057	5.611	97.73
Au/Ca-CeO2	3.50	80.378	4.599	19.622	1.017	5.616	97.82
Au/Ba-CeO2	3.50	60.031	3.434	39.969	2.071	5.505	95.56

Energy dispersive spectrometer (EDS): Elemental analysis of the catalysts before and after the reaction was carried out using an electron probe micro-analyzer (EPMA) instrument (JXA-8600 M, JEOL, Japan) equipped with an energy dispersive spectrometer (EDS). EPMA is widely used for in situ non destructive chemical analysis of minute solid samples. For the analysis, powder samples were first placed on a conductive carbon tape mounted on the sample holder and carbon coat was applied using JEOL JEE-420 Vacuum Evaporator. Quantitative analysis was performed using the EDS with a magnification of 65x and applied voltage of 15kV.

Table 11. Quantitative EDS analysis of dopants

Catalyst	% of dopant before reaction	% of dopant aftar reaction
Mg-CeO_2 (4mol % doped)	0.25	0.23
Ba-CeO_2 (4mol % doped)	3.57	2.27
Ca-CeO_2 (4mol % doped)	0.62	1.04

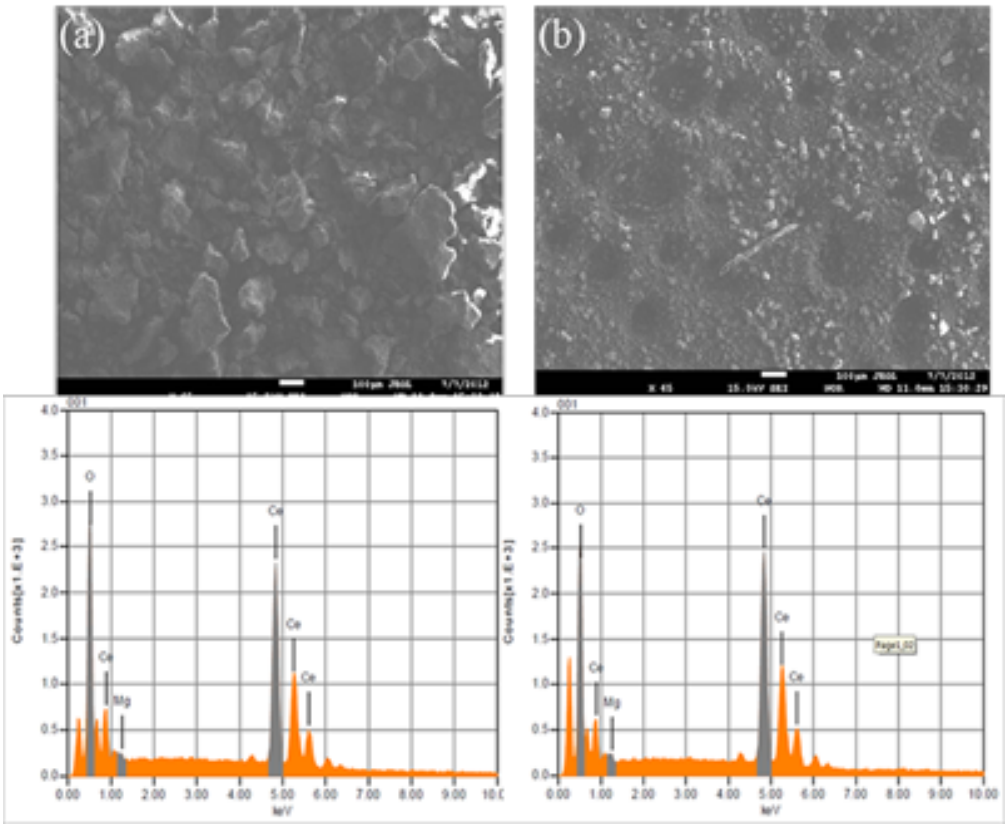

Fig. 14: EDS analysis of Mg-CeO_2 (Mg/Ce = 4/100) : (a) before reaction, (b) after reaction.

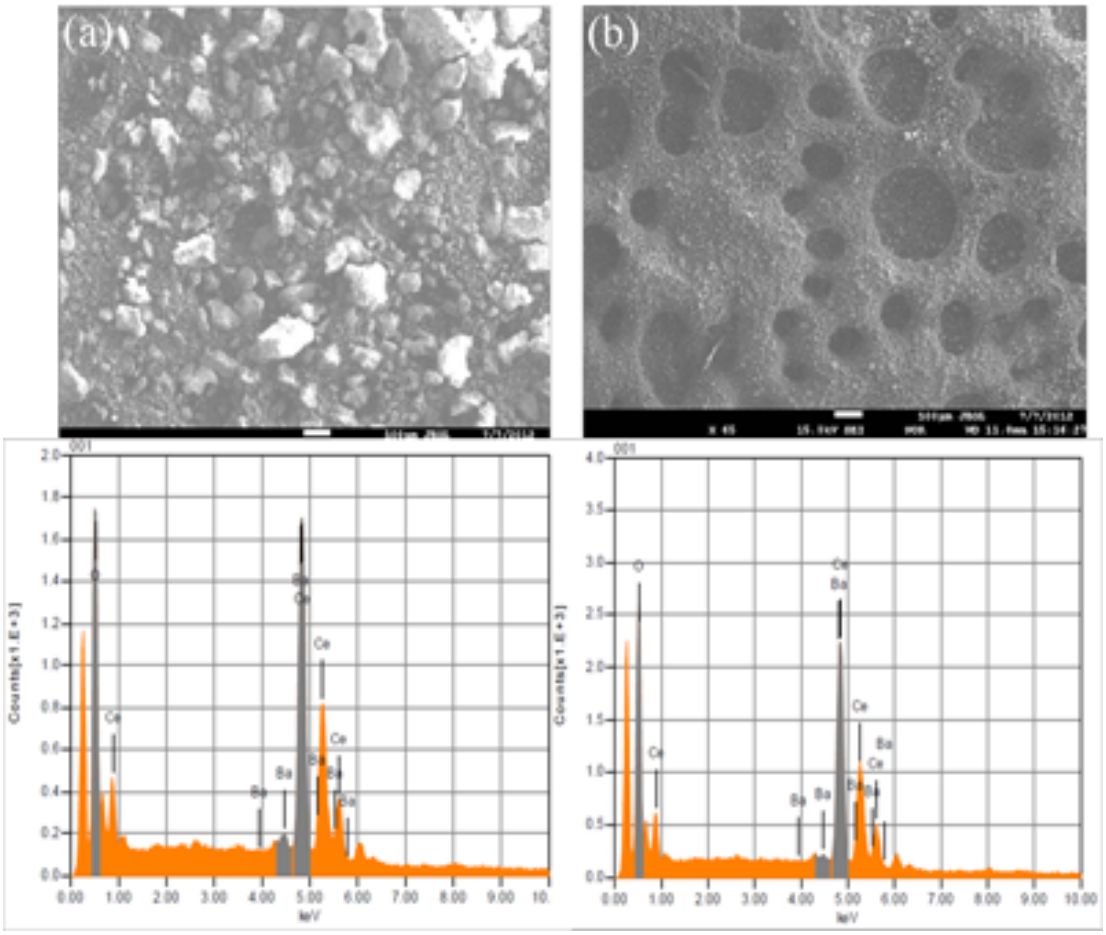

Fig. 15: EDS analysis of Ba-CeO_2 (Ba/Ce = 4/100) : (a) before reaction, (b) after reaction.

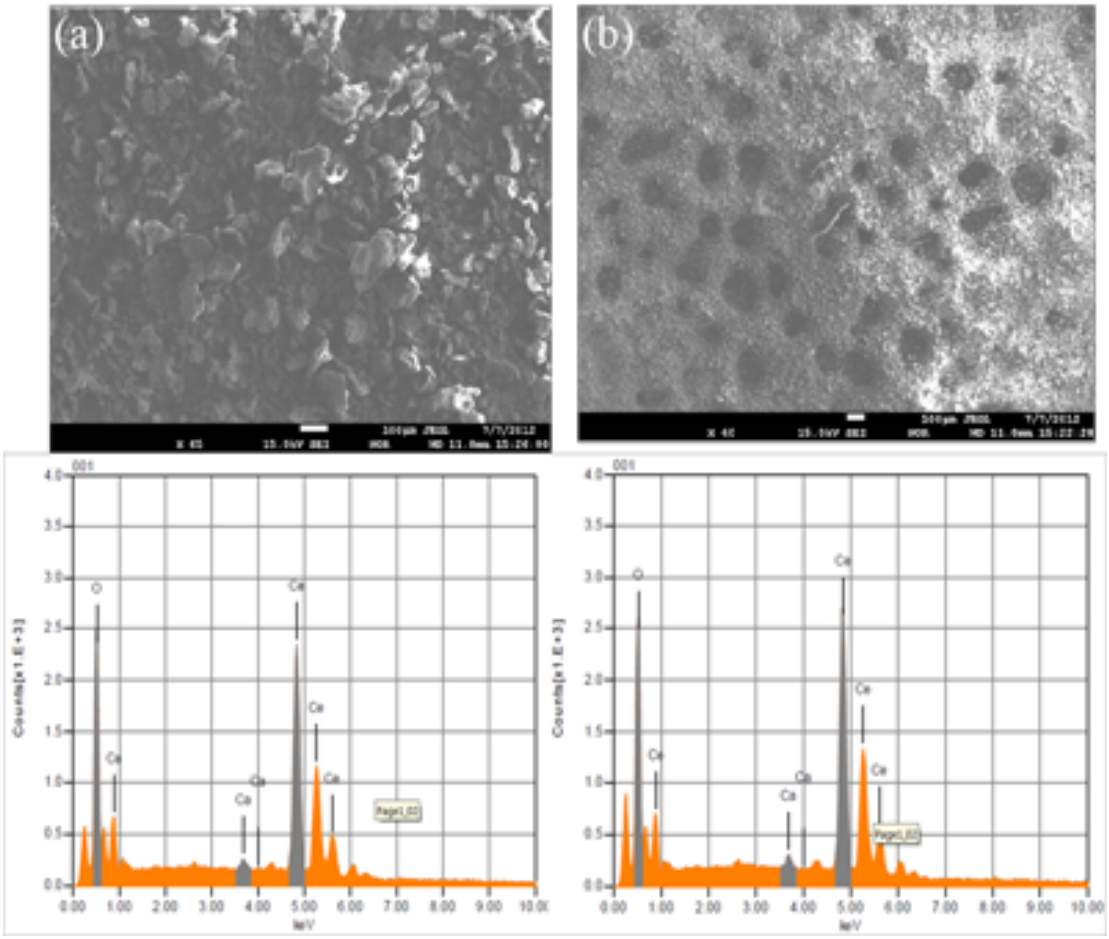

Fig. 16: EDS analysis of Ca-CeO_2 (Ca/Ce = 4/100) : (a) before reaction, (b) after reaction.