

## 1. Introduction

Phenol is an important chemical intermediate in industry owing to its widespread use. Industrially, phenol is produced by the three-steps cumene process, which involves an explosive cumene hydroperoxide intermediate, utilizes sulfuric acid and also suffers from low yield. Although there have been lots of reports using different oxidizing agents such as  $O_2$ ,  $N_2O$ ,  $H_2O_2$ ,  $NH_3+O_2$ , etc. on transition metal redoxcatalysts, most-desirable gas-phase single-step processes with good phenol yields have not been reported yet. We have found the unprecedented and novel aspects and mechanism of the selective oxidation catalysis for phenol production from benzene with high selectivity by single alkali and alkaline-earth metal-ionsites in zeolite pores with acid-base property.

## 2. Experimental

### 2.1 Catalyst preparation

Alkali and alkaline-earth metal/zeolite catalysts were prepared by an ion-exchange method. Typically, Cs/ $\beta$  was prepared as follows: 0.062 g of  $CsNO_3$  (Kanto Chemical Co., Inc.) was dissolved in 10 mL deionized water in an Erlenmeyer flask (50 mL), to which solution 1.96 g  $NH_4\beta$  with  $SiO_2/Al_2O_3 = 25$  (Nikki/Zeolyst) was added under stirring. For ion-exchange of  $NH_4$  ions with Cs ions, the solution was heated from room temperature to 353 K, and kept at 353 K for 12 h under stirring, followed by filtration under reduced pressure and washing with deionized water (500 mL) three times, and then drying at 353 K for 6 h to obtain Cs (2.1 wt%)/ $\beta$  samples.

### 2.2 Catalytic reaction set-up and product analysis

A given amount of the obtained sample (0.2 g) was charged in a continuous down-flow fixed-bed-flow glass reactor and pre-treated at 673 K for 0.5 h in a flow of  $Bz/O_2/NH_3/He = 0.5/0.5/1.8/4.0$  mL  $min^{-1}$  and cooled down rapidly to reaction temperatures (553-613K). The reaction products were analyzed by two on-line gas chromatographs (FID and TCD).

## 3. Results & Discussion

We conducted single-path gas-phase phenol synthesis reactions from benzene and  $O_2$  in the presence and absence of  $NH_3$  on various metal/zeolite catalysts. The performances of M/ $\beta$  (M: Cu, V, Pt, Ir, Ni, Mg, Na, K, Rb, and Cs;  $\beta$ :  $SiO_2/Al_2O_3=25$ ) catalysts for direct phenol synthesis from benzene and  $O_2$  in the presence of  $NH_3$  are listed in Table 1.

**Table 1.** Performances of various M/ $\beta$ zeolite catalysts for the direct phenol synthesis from benzene/ $O_2$  in the presence of  $NH_3$

Catalyst	Reac. temp. [K]	Benzene reac. rate [mmol h <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> ]	TOF [h <sup>-1</sup> ]	Phenol selec. [%]	$NH_3$ decomp. rate [mmol h <sup>-1</sup> g <sub>cat</sub> <sup>-1</sup> ]
Cu/ $\beta$ <sup>[a]</sup>	593	0.13	0.10	6.8	< 0.01
V/ $\beta$ <sup>[a]</sup>	553	< 0.002	-	-	1.2
Pt/ $\beta$ <sup>[b]</sup>	553	0.17	1.58	78.3	2.4
Ir/ $\beta$ <sup>[c]</sup>	573	0.20	1.93	89.0	1.5
Ni/ $\beta$ <sup>[a]</sup>	593	0.12	0.36	87.7	3.5
Mg/ $\beta$ <sup>[a]</sup>	593	0.08	0.47	84.0	0.89
Na/ $\beta$ <sup>[a,d]</sup>	593	0.08	0.44	93.0	< 0.2
K/ $\beta$ <sup>[a,d]</sup>	593	0.12	1.1	95.0	< 0.2
Rb/ $\beta$ <sup>[a,d]</sup>	593	0.17	3.5	96.0	1.4
Cs/ $\beta$ <sup>[a,d]</sup>	593	0.18	6.0	96.0	< 0.2
Cs/ $\beta$ <sup>[e]</sup>	593	0.09	3.0	3.5	-
Cs/ $SiO_2-Al_2O_3$ <sup>[a,d]</sup>	593	< 0.004	< 0.14	-	0.24

Cat= 0.2 g (M loading=2.1 wt%). [a] $Bz/O_2/NH_3/He=1.0/0.5/1.8/4.0$  mL  $min^{-1}$ . [b] $Bz/O_2/NH_3=0.5/1.6/8.0$  mL  $min^{-1}$ . [c]  $Bz/O_2/NH_3=1.0/0.5/1.8$  mL  $min^{-1}$ . [d]After calcination, further pretreated with  $Bz/O_2/NH_3/He=1.0/0.5/1.8/4.0$  mL  $min^{-1}$  at 673 K for 30 min. [e] $Bz/N_2O/NH_3/He=1.0/0.5/1.8/4.0$  mL  $min^{-1}$ .

The combustions of benzene and  $NH_3$  with  $O_2$  on Pt/ $\beta$ , Ir/ $\beta$  and Ni/ $\beta$  occurred rapidly, whereas the benzene- $O_2$  reaction pathway was switched over from the deep oxidation to the selective hydroxylation with the phenol selectivity of 78.3-89.0% by coexisting  $NH_3$ . On alkali metal/ $\beta$  and alkaline earth metal/ $\beta$ , benzene

and  $\text{NH}_3$  did not react with  $\text{O}_2$  significantly, but in the three component system of benzene/ $\text{O}_2$ / $\text{NH}_3$  the benzene oxidation to phenol proceeded selectively (84.0-96.0% selectivity) (Table 1).

Thereafter, I screened several alkali and alkaline earth metals/ $\beta$  catalysts in benzene oxidation reactions and their reactivity is tabulated in Table 2.

**Table 2.** Performances of alkali and alkaline-earth metal/ $\beta$  catalysts in the synthesis of phenol from benzene/ $\text{O}_2$ ,  $\text{NH}_3$ <sup>[a]</sup>.

Catalyst	Benzene Conversion [%]	Benzene reaction rate [ $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ]	TOF [ $\text{h}^{-1}$ ]	Phenol Selectivity [%]	$\text{NH}_3$ reaction rate [ $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ]	$[\text{NH}_3]_{\text{reacted}}/[\text{Phenol}]_{\text{produced}}$
$\beta$ -zeolite	0.0	0	0	0	0	-
Mg/ $\beta$	0.6	0.08	0.47	84	0.89	13
Ca/ $\beta$	0.5	0.07	0.61	78	0.90	17
Sr/ $\beta$	0.5	0.07	1.47	81	1.20	21
Ba/ $\beta$	0.5	0.06	2.01	78	1.20	23
Na/ $\beta$	0.6	0.08	0.44	93	0	0
K/ $\beta$	0.9	0.12	1.12	95	0	0
Rb/ $\beta$	1.3	0.17	3.5	96	1.36	8.3
Cs/ $\beta$	1.3	0.18	6.0	96	0.04	0.4
Cs/Mordenite	0.0572	0.008	0.25	99	0.1	0.8
Cs/ $\text{SiO}_2\text{Al}_2\text{O}_3$	0.02	0.002	0.07	76.5	0.24	228.8

[a] Reaction Conditions: catalyst (metal loading = 2 wt %) amount: 0.2 g; reaction temperature = 593K; time = 30-180 min; benzene/ $\text{O}_2$ / $\text{NH}_3$ /He = 1.0: 0.5: 1.8 :4 mL/min. The catalysts were pretreated with benzene/ $\text{O}_2$ / $\text{NH}_3$ /He (1.0: 0.5: 1.8 :4 mL/min) 673 K for 0.5h. TOF are defined as reacted benzene/total metal per hour. All zeolites were purchased from Zeolyst International Company.

To our surprise, we observed that, the alkali metals displayed higher selectivities (> 80%) towards phenol production. Moreover, Rb and Cs-based  $\beta$  catalysts also showed greater conversions. But, using Cs/ $\beta$  catalyst, decomposition of  $\text{NH}_3$  was drastically diminished. However, in their bi-component system (benzene +  $\text{O}_2$ ) without  $\text{NH}_3$ , no benzene oxidation (Table 3).

**Table 3.** Catalytic performances of Cs/ $\beta$  zeolites in the synthesis of phenol from benzene<sup>[a]</sup>.

Conditions [At Steady State Reaction]	Benzene reaction rate [ $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ]	TOF [ $\text{h}^{-1}$ ]	Phenol Selectivity [%]	$\text{NH}_3$ reaction rate [ $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ]
Benzene + $\text{O}_2$ + $\text{NH}_3$	0.18	6.0	96	0.04
Benzene + $\text{O}_2$	0	0	0	0
Benzene + $\text{NH}_3$	0	0	-	0.7
$\text{NH}_3$ + $\text{O}_2$	-	-	-	0.4
Benzene + $\text{O}_2$ + Propylamine	0	0	0	0
Benzene + $\text{O}_2$ + Pyridine	0	0	0	0

[a] Reaction Conditions: catalyst = Cs (2wt%/ $\beta$ ); catalyst amount: 0.2 g; reaction temperature = 593K; time = 30-180 min; benzene/ $\text{O}_2$ / $\text{NH}_3$ /He = 1.0: 0.5: 1.8 :4 mL/min; The catalysts were pretreated with benzene/ $\text{O}_2$ / $\text{NH}_3$ /He (1.0: 0.5: 1.8 :4 mL/min) 673 K for 0.5h.



However, we observed that, under the present condition, conversion of benzene was still < 5% and we performed several reactions, in order to get better yields for phenol (Table 4).

**Table 4.** Catalytic performances of Cs/ $\beta$  ( $\beta$ =Zeolyst International) catalysts in the synthesis of phenol from benzene/O<sub>2</sub>, regulated by NH<sub>3</sub> at 593K<sup>[a]</sup>

Cat Wt. [g]	Benzene flow [mlmin <sup>-1</sup> ]	NH <sub>3</sub> Decomp [%]	Benzene Conv. [%]	Phenol Select. [%]	Benzene reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	Phenol formation rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	TOF [h <sup>-1</sup> ]	NH <sub>3</sub> reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	NH <sub>3</sub> reacted/ Phenol formed
0.2	1	0.2	0.4	86.5	0.0149	0.0129	1.70	0.0134	1.03
0.2	0.75	0.2	1.04	90.3	0.0292	0.0263	3.32	0.0134	0.51
0.2	0.5	1.2	1.6	79.2	0.0299	0.0237	3.41	0.0804	3.4
0.3	1	0.3	0.88	85.0	0.0219	0.0185	1.66	0.0134	0.72
0.3	0.75	0.1	1	89	0.0187	0.0166	1.42	0.0044	0.27
0.3	0.5	0.6	2.6	76.4	0.0324	0.0247	2.46	0.0267	1.08
0.6	1	0.4	1.3	86	0.0162	0.0140	0.62	0.0089	0.64
0.6	0.75	0.9	2.4	77	0.0225	0.0173	0.85	0.0201	1.16
0.6	0.5	1.3	3.4	67	0.0211	0.0141	0.804	0.0291	2.05
0.8	1	0.55	1.6	81	0.0149	0.0121	0.43	0.0092	0.76
0.8	0.75	1.4	2.5	74	0.0175	0.0130	0.50	0.0234	1.8
0.8	0.5	2.8	7.1	41.5	0.0332	0.0138	0.95	0.0468	3.4
1	1	1.8	3.8	54	0.0284	0.0154	0.65	0.0241	1.57
1	0.75	3.2	3.7	55	0.0207	0.0114	0.47	0.0428	3.75
1	0.5	3.4	4.4	37.4	0.0163	0.0061	0.37	0.0455	7.43

[a] Reaction Conditions: catalyst = Cs (2.1 wt%)/ $\beta$ ; reaction temperature= 593K; time=30-180 min; benzene/O<sub>2</sub>/NH<sub>3</sub>/ He =1.0: 0.5: 1.8 :4 mL/min; The catalysts were pretreated with benzene/O<sub>2</sub>/NH<sub>3</sub>/ He (1.0: 0.5: 1.8 :4 mL/min) 673 K for 0.5h. TOF are defined as reacted benzene/total metal per hour.  $\beta$  zeolites were purchased from Zeolyst International.

It was observed that taking 0.6g Cs/ $\beta$  catalyst ( $\beta$  from Zeolyst company), and adjusting the flow of benzene (0.75mlmin<sup>-1</sup>) the conversion of benzene was rose to 2.4%. Thereafter, I tried to study the effect of Cs-precursors in the benzene oxidation reaction (Table 5).

**Table 5.** Performances of Cs/ $\beta$ catalysts in the synthesis of phenol from benzene/O<sub>2</sub>, regulated by NH<sub>3</sub> at 593K, using various precursors of Cs<sup>[a]</sup>

Cs-Precursors	NH <sub>3</sub> Decom [%]	Benzene Conv. [%]	Phenol Select. [%]	Benzene reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	Phenol formation rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	TOF [h <sup>-1</sup> ]	NH <sub>3</sub> reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	NH <sub>3</sub> reacted/ Phenol formed
CsNO <sub>3</sub>	0.9	2.4	77	0.02249	0.0173	0.853	0.0201	1.16
Cs <sub>2</sub> CO <sub>3</sub>	0.74	1.1	75.3	0.01012	0.0076	0.384	0.0165	2.2
CsCl	1.22	0.5	81.0	0.00468	0.0038	0.178	0.0272	7.2
CsOH	1.20	1.4	83.0	0.01312	0.0109	0.498	0.0268	2.5

[a] Reaction Conditions: catalyst = Cs (2.1 wt%)/ $\beta$  ( $\beta$ = Zeolyst International); catalyst weight = 0.6g; reaction temperature= 593K; time=30-180 min; benzene/O<sub>2</sub>/NH<sub>3</sub>/ He =0.75: 0.5: 1.8 :4 mL/min; The catalysts were pretreated with benzene/O<sub>2</sub>/NH<sub>3</sub>/ He (0.75: 0.5: 1.8 :4 mL/min) 673 K for 0.5h. TOF are defined as reacted benzene/total metal per hour.

Notably, the catalytic performance largely depended-on the source of Cs and the type of zeolite. CsNO<sub>3</sub> was proved to be the best and CsOH was the worst one. The reason behind this observation may lead to the fact that, CsNO<sub>3</sub>, which is highly ionic dissolves thoroughly in water medium and during the ion-exchange process, and perhaps the Cs ions are therefore can be effectively transferred to the catalyst surface; whereas CsOH, bearing higher degree of covalency fails to transfer effective Cs ions on the catalyst surface.



Then we purchased  $\beta$ -zeolites from various companies and prepared Cs-based catalyst and performed benzene oxidation reactions under the same conditions (Table 6).

**Table 6.** Performances of Cs/ $\beta$ catalysts in the synthesis of phenol from benzene/O<sub>2</sub>, regulated by NH<sub>3</sub> at 593K, using various  $\beta$ -zeolite source<sup>[a]</sup>

Source of $\beta$ -Zeolite	NH <sub>3</sub> Decom [%]	Benzene Conv. [%]	Phenol Select. [%]	Benzene reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	Phenol formation rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	TOF [ $\text{h}^{-1}$ ]	NH <sub>3</sub> reaction rate [ $\mu\text{mol s}^{-1}\text{g}_{\text{cat}}^{-1}$ ]	NH <sub>3</sub> reacted/ Phenol formed
Zeolyst	0.9	2.4	77	0.02249	0.01732	0.853	0.02012	1.16
Zeolyst*	1.3	3.4	67	0.0211144	0.0141444	0.801	0.02907	2.05
NIKKI	0.4	2.10	82.2	0.01967	0.0162	0.747	0.00894	0.55
NIKKI*	1.51	5.89	83.4	0.03679	0.0307	1.397	0.03377	1.10
TOSOH	0.76	0.42	85.4	0.00393	0.00336	0.149	0.01699	5.06
Clariant	0.63	0.06	88.3	0.00056	0.00050	0.021	0.01409	2.84

[a] Reaction Conditions: catalyst = Cs (2.1 wt%)/ $\beta$ ; catalyst weight = 0.6g; reaction temperature= 593K; time=30-180 min; benzene/O<sub>2</sub>/NH<sub>3</sub>/ He =0.75: 0.5: 1.8 :4 mL/min; The catalysts were pretreated with benzene/O<sub>2</sub>/NH<sub>3</sub>/ He (0.75: 0.5: 1.8 :4 mL/min) 673 K for 0.5h. TOF are defined as reacted benzene/total metal per hour.  
\*Benzene/O<sub>2</sub>/NH<sub>3</sub>/He =0.5/ 0.5/1.8/4.0 mL min<sup>-1</sup>

Among them, the catalysts prepared using  $\beta$ -zeolites Nikki showed the best performance and used to carry out the other reactions (Table 7).

**Table 7.** Catalytic performances of Cs/ $\beta$  ( $\beta$  = Nikki) catalysts in the synthesis of phenol from benzene/O<sub>2</sub>, regulated by NH<sub>3</sub><sup>[a]</sup>

Catalyst Wt. [g]	Benzene flow [ml/min]	NH <sub>3</sub> Decom [%]	Benzene Conv. [%]	Phenol Select. [%]	Benzene reaction rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	Phenol formation rate [ $\mu\text{mol s}^{-1}\text{g}^{-1}_{\text{cat}}$ ]	TOF [ $\text{h}^{-1}$ ]	NH <sub>3</sub> reaction rate [ $\mu\text{mol s}^{-1}\text{g}_{\text{cat}}^{-1}$ ]	NH <sub>3</sub> reacted/ Phenol formed
0.2	0.75	0.32	1.20	96.8	0.03366	0.0326	3.835	0.0214	0.658
0.2	0.5	0.04	1.64	98.4	0.03067	0.0302	3.494	0.0003	0.0088
0.3	0.75	0.38	1.33	95.7	0.02485	0.0238	1.887	0.0169	0.71
0.3	0.5	0.84	2.40	94.2	0.02952	0.0278	2.242	0.0370	1.33
0.5	0.75	0.58	2.40	94.1	0.02671	0.0251	1.217	0.0155	0.618
0.5	0.5	0.98	3.71	80.8	0.02775	0.0224	2.108	0.0262	1.17
0.8	0.75	0.78	3.21	87.2	0.02251	0.0196	0.641	0.0130	0.66
0.8	0.5	2.93	4.60	78.0	0.02151	0.0168	0.612	0.0490	2.93
1.0	0.75	0.5	3.20	81.5	0.01795	0.0146	0.409	0.0067	0.46
1.0	0.5	1.25	6.85	64.5	0.02562	0.0165	0.583	0.0167	1.01
0.6	0.75	0.81	2.56	91.8	0.02399	0.0220	0.911	0.0181	0.82
0.6	0.5	1.51	5.89	83.4	0.03679	0.0307	1.397	0.0337	1.10
0.6	0.25	1.74	4.40	87.0	0.01374	0.0120	0.522	0.0389	3.3
0.6 <sup>[b]</sup>	0.5	1.08	2.86	99.8	0.01786	0.0178	1.424	0.0241	1.35
0.6 <sup>[c]</sup>	0.5	1.05	4.26	90.1	0.02661	0.0240	0.707	0.0235	0.98
0.6 <sup>[d]</sup>	0.5	1.38	3.94	69.7	0.02461	0.0172	0.392	0.0308	1.80
0.6 <sup>[e]</sup>	330	2.90	6.26	85.1	0.03910	0.0333	1.485	0.0648	1.95
0.6 <sup>[f]</sup>	350	3.33	6.84	77.5	0.04272	0.0331	1.622	0.0745	2.25

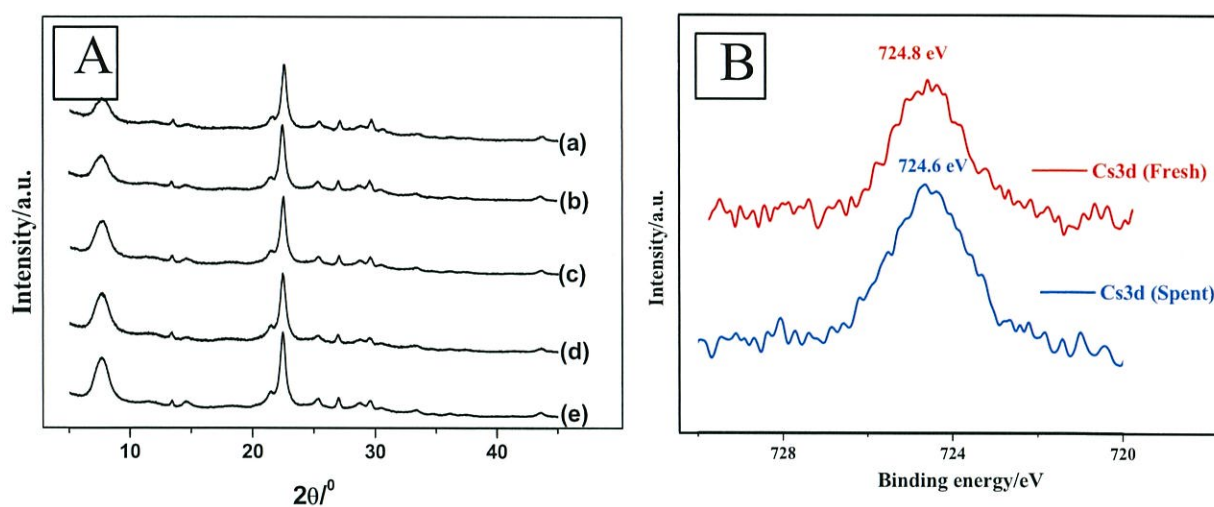
[a] Reaction conditions: catalyst = Cs (2.1 wt%) / $\beta$  ( $\beta$ = Nikki) amount: 0.2 g; reaction temperature= 593K; time=30-180 min; O<sub>2</sub>/NH<sub>3</sub>/ He = 0.5: 1.8 :4 mL/min; The catalysts were pretreated with benzene/O<sub>2</sub>/NH<sub>3</sub>/He 673 K for 0.5h. TOF are defined as reacted benzene/total metal per hour. Loading of Cs [b] 1 wt%; [c] 3 wt%; [d] 5 wt%. Reaction temperature [e] 330 °C and [f] 350 °C.

It was noticed that, increment in catalyst weight and lowering the flow of benzene (0.5mL min<sup>-1</sup>), the increment in the conversion of benzene occurred. When the weight of the catalyst was 1 g, and flow of benzene was 0.5mL min<sup>-1</sup>, the conversion of benzene was 7%, although, selectivity to phenol was 64%.

Then I took 0.6 g catalyst, without hampering other conditions and 6% benzene conversion, with selectivity to phenol was 84%. Moreover, I also noticed that, Cs-loading also played an important role in this reaction. Increment in loading of Cs led to the decrement in phenol yield, probably due to the fact that, increment in Cs loading decreased the effective Cs-ions on the catalyst surface and the Cs<sup>+</sup> ions that reside in the bulk are not responsible for the catalysis. Reaction temperature too had an effect on the benzene oxidation reaction. Increment in reaction temperature from 320 °C to 350 °C, the conversion of benzene rose to 7%, although at that temperature, increment in the conversion of NH<sub>3</sub> also increased.

#### 4. Catalyst Characterization

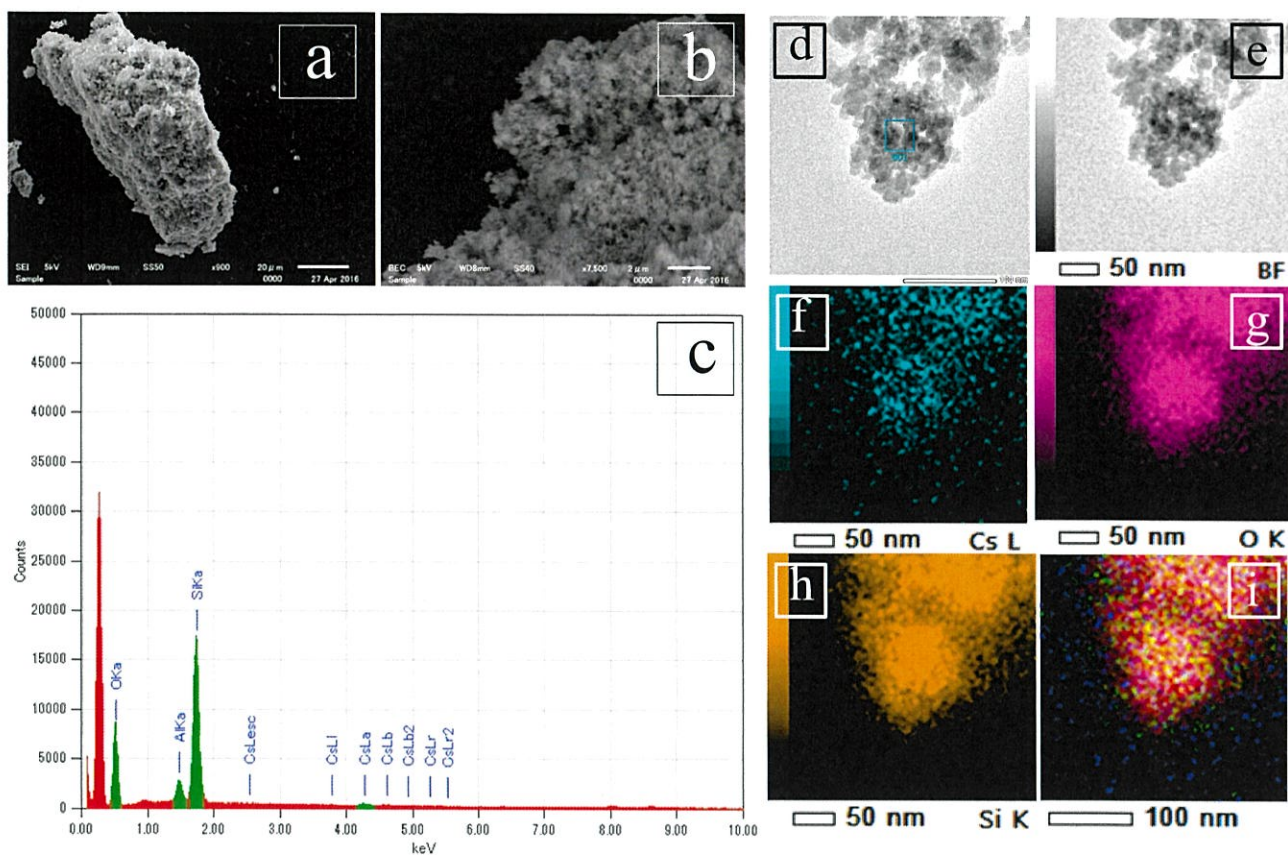
In order to know the oxidation state of Cs, we carried out XRD of the catalyst (Fig. 1a). But we could not differentiate the XRD diffractogram of the catalyst from the bare support (zeolite). Therefore, we compelled to do its XPS analysis in order to know the oxidation state of Cs-species (Fig. 1b).



**Fig. 1(A).** XRD diffractogram of Cs/ $\beta$  catalyst with (a) 10 wt% Cs loading, (b) 5 wt% Cs loading, (c) 2 wt% Cs loading (fresh), (d) 2 wt% Cs loading (spent) and that of (e)  $\beta$ -zeolite; **(B)** Cs 3d<sub>5/2</sub> binding energy of fresh and spent Cs/ $\beta$  catalyst.

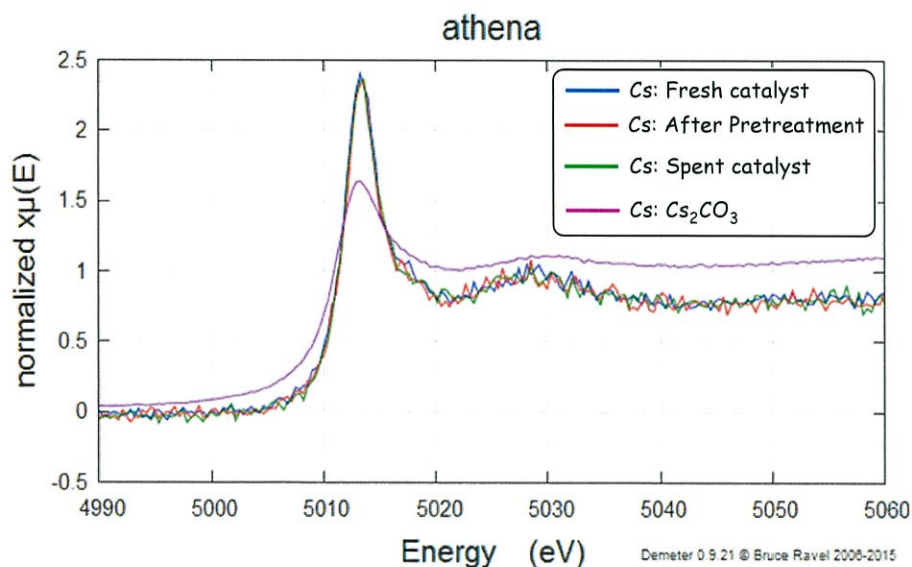
The 3d<sub>5/2</sub> binding energy for the fresh catalyst is 724.8 eV and that in the spent is 724.6 eV which actually demonstrated the monocationic nature of the Cs-species in the catalyst. Being interested to know the morphology of the catalyst, we measured SEM images of the catalyst (Fig. 2). No definite morphology of the catalyst was speculated; although poor signal due the presence of Cs was observed from SEM-EDS. To locate the position of Cs, the catalyst was gone through TEM and STEM. From the elemental mapping of the TEM image, we visualized the presence of Cs and as well as the other elements. The image also depicts that, probably, the Cs-species are highly dispersed-over the beta-zeolite.





**Fig. 2** SEM image (a/b) of the Cs/ $\beta$  catalyst with different magnifications; (c) the corresponding SEM-EDS image; (d) STEM image and (e) the corresponding TEM image and the TEM-elemental mapping of (f) Cs, (g) O and (h) Si in the selected TEM image of the Cs/ $\beta$  catalyst.

X-ray absorption fine structure (XAFS) was used to further probe the chemical state and coordination structure of the Cs-species in the catalyst. The performed in-situ Cs  $L_3$ -edge X-ray absorption near-edge structure (XANES) (Fig. 3) was in contrast with that obtained from XPS analysis.



**Fig. 3** XANES spectra at Cs LIII-edge for the Cs-supported: (—) fresh, (—) pre-treated, (—) spent catalyst and that of (—)  $\text{Cs}_2\text{CO}_3$ .

The XANES of the pre-treated catalyst was same as that of the fresh and the spent one, demonstrating the fact that, the valence state remains the same in all the mentioned cases. But these white line intensities were very different to that of commercial  $\text{Cs}_2\text{CO}_3$ . This anomaly behavior of Cs-species in the catalyst can be attributed to the presence of vacant d-orbitals in Cs and thus, local coordination is different to that of  $\text{Cs}_2\text{CO}_3$ . This experimental finding was further confirmed from extended X-ray fine structure (EXAFS) analyses Table 8.

**Table 8.** Summary of the EXAFS fitting results for Cs/ $\beta$ catalysts

Catalyst	Path	CN	$\Delta E_0$	R	DW	R-factor
Cs/ $\beta$ <sup>[a]</sup>	Cs-O	3.86 $\pm$ 2.07	-3.06 $\pm$ 3.42	3.06 $\pm$ 0.05	0.0015 $\pm$ 0.0106	0.0032
Cs/ $\beta$ <sup>[b]</sup>	Cs-O	3.69 $\pm$ 3.81	-0.59 $\pm$ 8.13	3.20 $\pm$ 0.17	0.0017 $\pm$ 0.0314	0.0337
Cs/ $\beta$ <sup>[c]</sup>	Cs-O	3.92 $\pm$ 13.65	-4.82 $\pm$ 26.64	3.03 $\pm$ 0.36	0.0000 $\pm$ 0.0525	0.1624
[a] Fresh Cs(2.1 wt%)/ $\beta$ catalyst, [b] the catalyst after pretreatment and [c] spent catalyst.						

The Cs  $L_3$ -edge EXAFS also revealed that the coordination number (CN) of Cs in the fresh catalyst and that after the steady-state reaction is about 4, which states that one Cs atom is surrounded by 4 oxygen atoms; moreover, Cs-O distance is 3.03-3.20 Å. These data are in accordance with the fact that, there is no Cs-Cs bond. That means Cs-species in the catalyst is single metal ions. EXAFS also depicts the fact that, no change in the catalyst occurs when the catalyst is pre-treated under 400°C and even after catalysis.–

#### 4. Conclusions

The Cs/ $\beta$ -zeolite catalyst afforded direct benzene-to-phenol oxidation with 75-85% phenol selectivity at benzene conversions of 5-8% in presence of  $\text{NH}_3 + \text{O}_2$  in a single-step gas-phase fixed-bed down-flow reactor. The catalysts were characterized by XAFS, XPS, STEM-EDS, XRD, SEM, TEM, etc. The present finding signifies that acid-base catalysis can promote selective oxidation reactions unlike the traditional common concept.



10. Research Presentations during the period of the fellowship (Name of the conference, title, place, date)

1. Poster presentation on Unexpected Selective Oxidation of Benzene to Phenol by Alkali- and Alkaline-Earth Metal/Zelite Catalysts at International Symposium on Novel Energy Nanomaterials, Catalysts and Surfaces for Future Earth [NENCS], The University of Electro-Communications, Japan, 28-30<sup>th</sup> October 2017.
2. Attended **97th CSJ Annual Meeting** at Yokohama, Japan, 16<sup>th</sup> March 2017.
3. Oral presentation on Selective Switchover of the Catalytic Reaction Pathways from Complete Oxidation to Selective Hydroxylation of Benzene on Alkali and Alkaline Earth Metals/Zelolites at The 16<sup>th</sup> International Congress on Catalysis [ICC 16], Beijing, China, 3-8<sup>th</sup> July 2016.
4. Oral presentation on Highly Selective Direct Synthesis of Phenol from Benzene and O<sub>2</sub> Regulated by NH<sub>3</sub> on Alkali and Alkaline Earth Metals/Zelolites at **96th CSJ Annual Meeting**, Kyotanabe Campus, Doshisha University, Kyoto, Japan, 24-27<sup>th</sup> March 2016.

11. A list of paper published during or after the period of the fellowship, and the names of the journals in which they appeared (Please fill in the format below). Attach a copy of each article if available.

Author(s)	Title	Name of Journal	Volume	Page	Date	Note
Y. Iwasawa, S. Yamamoto, L. Wang, K. Hayashizaki, <b>S. S. Acharyya</b> , S. Ghosh, Method of Phenol Production [フェノールの製造方法 JP 2017-81916A 2017.5.18] <b>Japanese Patent, Application No. 特願2016-211810</b>						

12. Awards during the period of the fellowship (Name of the award, Institution, date etc.)

**Poster Award** at International Symposium on Novel Energy Nanomaterials, Catalysts and Surfaces for Future Earth [NENCS] for the paper Unexpected Selective Oxidation of Benzene to Phenol by Alkali- and Alkaline-Earth Metal/Zelite Catalysts, Japan, 2017.