Supporting Information

Confined Single Alkali Metal Ion Platform in Zeolite Pore for Concerted Benzene C–H Activation-to-Phenol Catalysis

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Table S1: Performances of catalysts for the gas-phase hydroxylation of benzene to phenol in the literature

Catalyst	Oxidant	Reaction Condition	Benz Conv (%)	Phenol Select (%)	Reference
Fe/ ZSM5 catalysts	N_2O	Temperature= 350°C-400°C	20-30	99	*Appl. Catal. A: Gen,* **1992**, *82*,31
Cu/ZSM-5 catalyst	O_2	Temperature= 400 ^{0}C	2.0	60	*J. Mol. Catal.* A **2002**, *178*, 89.
FeAlPO-5	N_2O	Temperature= 380°C	13.4	97	*Chem. Commun.* **2006**, 4955
Interstitial-N/Re Cluster/Zeolite	O_2 +NH_3	Temperature= 280°C	0.8	88	*Angew. Chem.* **2006,** *45*, 448
VxOy@C-0.195–120	O_2	Temperature= 80 °C Pressure(O_2)= 3.0 MPa	13.0	93.8	*Green Chem.* **2013**,*15,* 1150-1154
10% Pd-VOx Nanoparticles	O_2	Temperature= 140 °C Pressure= 2.0 MPa	4.5	99	*ChemPlusChem* **2014,** *79*, 680
Pt-Re/ZSM-5	O_2 +NH_3	Temperature= 260°C	13	78	*ChemCatChem* **2013**, *5*, 2203
Ir/β	O_2 +NH_3	Temperature= 300°C	12	70	*ChemCatChem* **2015**, *7*, 3248
Cu(II)/$CuCr_2O_4$ Nanoparticles	Air	Temperature= 350 °C Pressure (air)= 3.5 MPa	36	78	*ACS Catal.* **2015**, *5,* 2850
Fe/ZSM-5 nanosheet	N_2O	Temperature=350°C	27.9	99	*ACS Catal.* **2017**, *7,* 2709
Meso-Fe-ZSM-5	N_2O	Temperature=320°C Pressure= 101 kPa.	22.1	100	*Catal. Sci. Technol.,* **2011**, *1*, 1250
Cs/β zeolite	O_2 +NH_3	Temperature=320°C	5.9	83.4	This Work
Rb/β zeolite	N_2O	Temperature=300°C	25.5	99.9	This Work

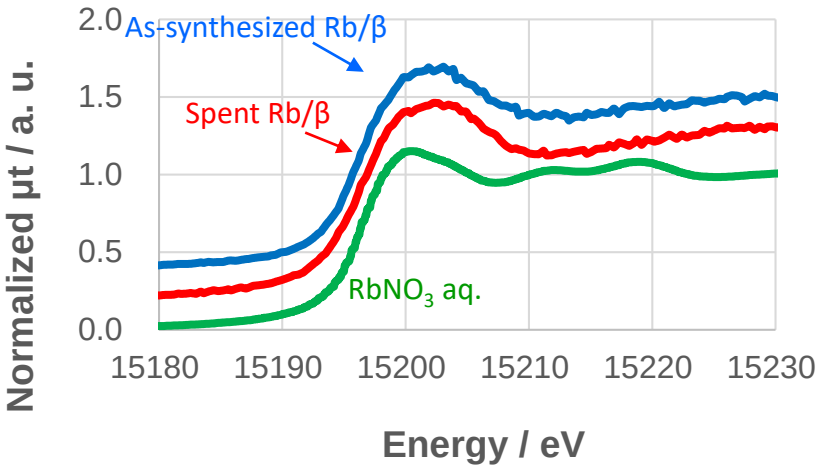


Figure S1. *In situ* Rb K-edge XANES spectra. Blue: fresh (as-synthesized) Rb/β catalyst. Red: spent Rb/β catalyst. Green: $RbNO_3$ reference. $RbNO_3$ aq. from A. Mihelič, A. Kodre, I. Arčon, J. P. Gomilšek, *Acta Chim. Slov.* 51, 33 (2004).

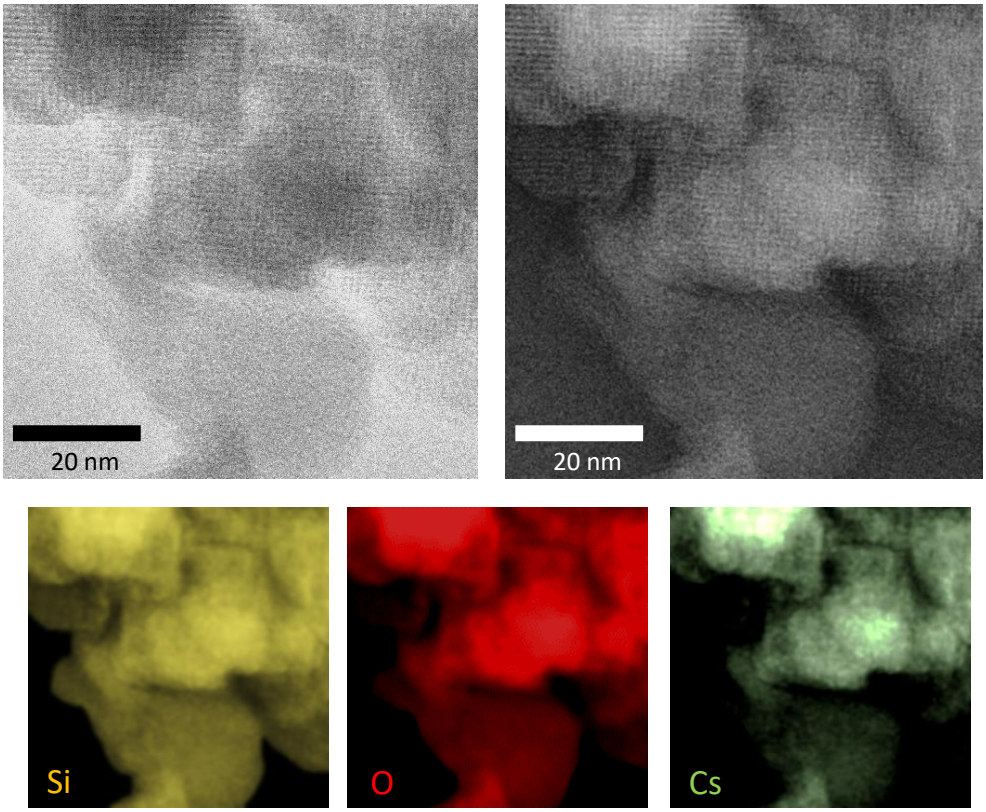


Figure S2. Bright and dark fields STEM images and elements (Si, O and Cs) mapping for Cs(2 wt%)/β. The bright and dark fields STEM images reveal no images except for the β zeolite lattice.

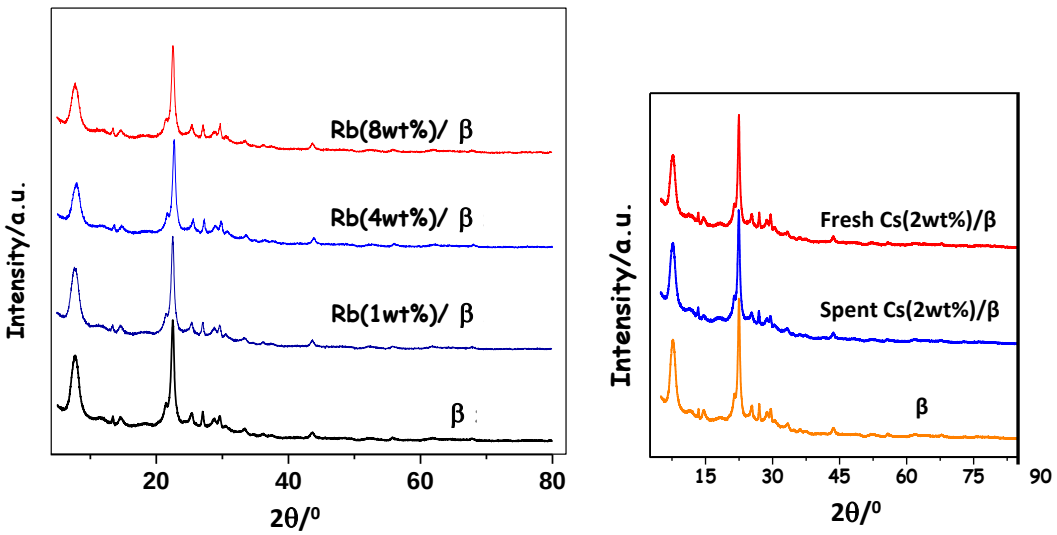


Figure S3. XRD patterns for Rb/β and Cs/β catalysts. They are similar to XRD pattern of β. There are neither Rb oxides nor Cs oxides.

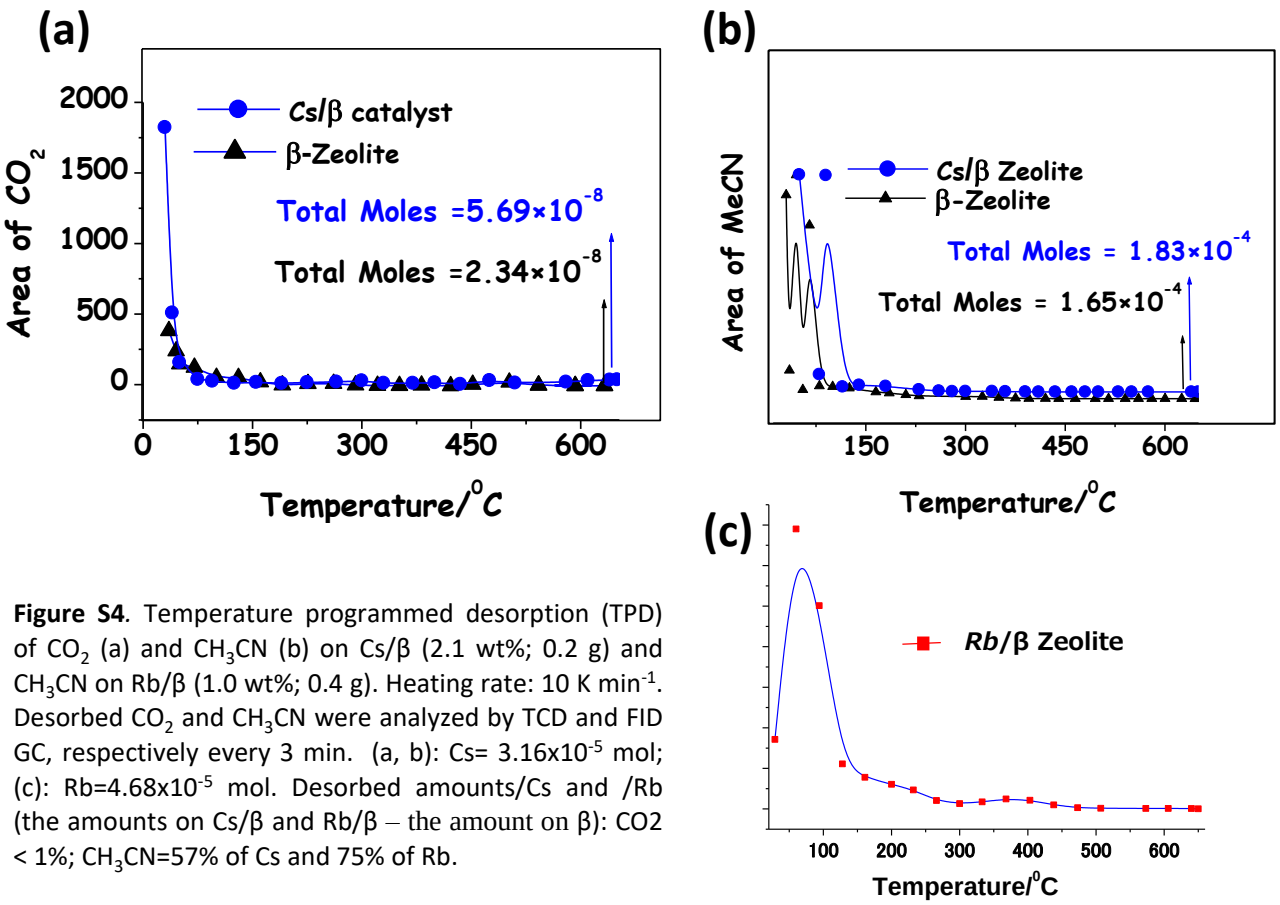


Figure S4. Temperature programmed desorption (TPD) of CO_2 (a) and CH_3CN (b) on Cs/β (2.1 wt%; 0.2 g) and CH_3CN on Rb/β (1.0 wt%; 0.4 g). Heating rate: 10 K min^{-1}. Desorbed CO_2 and CH_3CN were analyzed by TCD and FID GC, respectively every 3 min. (a, b): Cs= 3.16x10^{-5} mol; (c): Rb=4.68x10^{-5} mol. Desorbed amounts/Cs and /Rb (the amounts on Cs/β and Rb/β – the amount on β): CO2 < 1%; CH_3CN=57% of Cs and 75% of Rb.

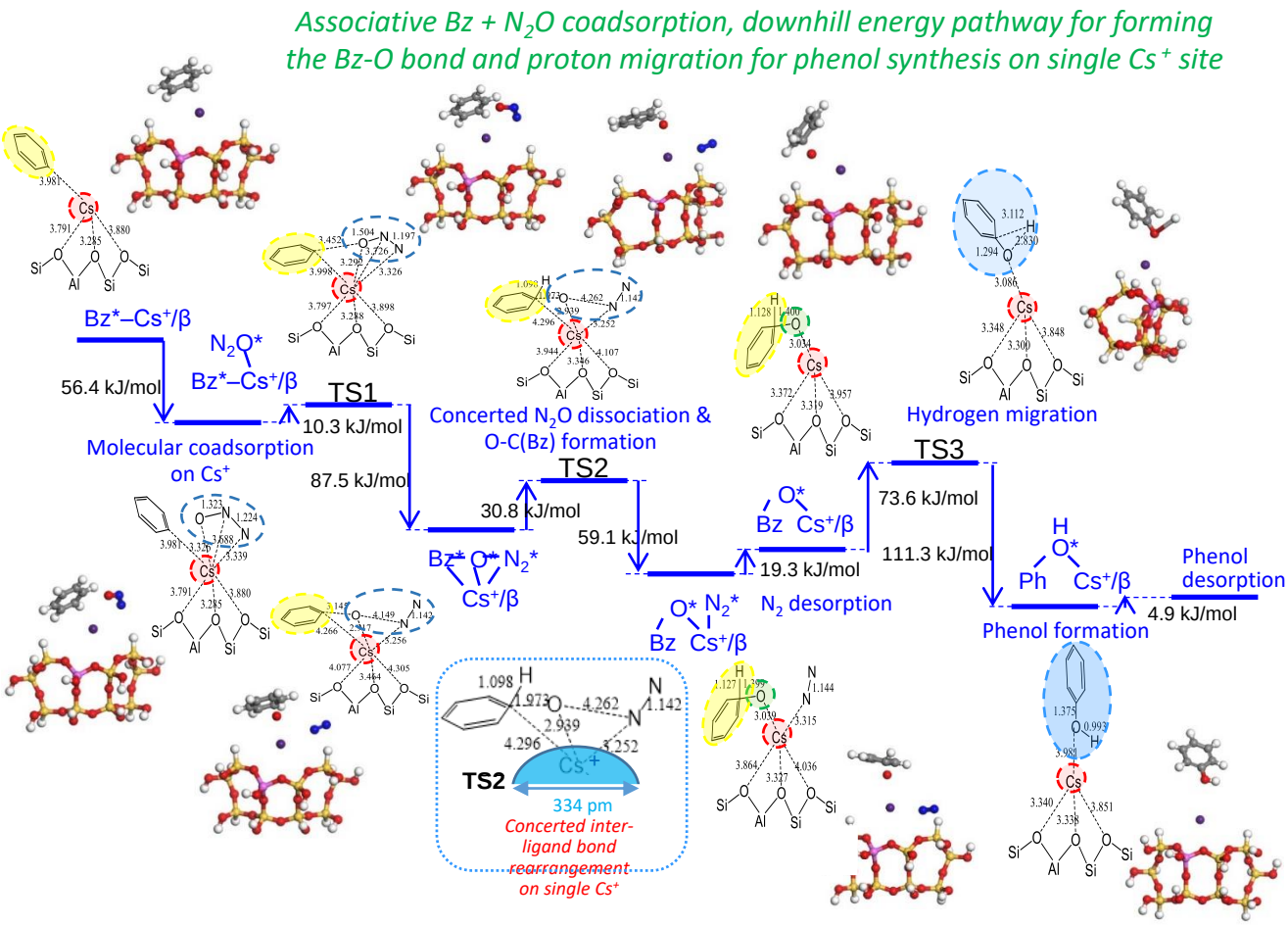


Figure S5. A computational downhill-energy reaction profile for the concerted inter-ligand reaction mechanism involving coadsorption and transition states for the selective oxidation of benzene to phenol with N_2O on the Cs^+/β cluster by DFT calculations. Asterisks(*) imply direct interaction with Cs^+.

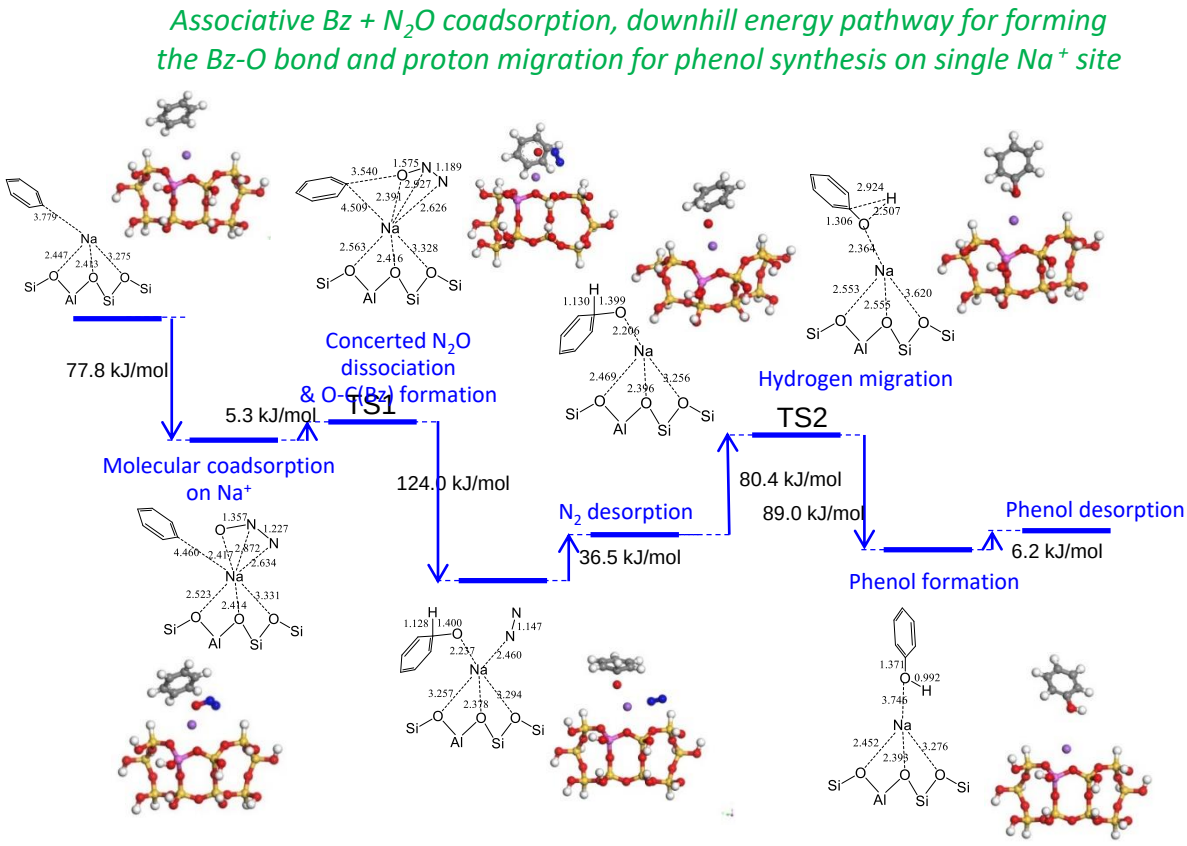


Figure S6. A computational downhill-energy reaction profile for the concerted inter-ligand reaction mechanism involving coadsorption and transition states for the selective oxidation of benzene to phenol with N_2O on the Na^+/β cluster by DFT calculations. Asterisks(*) imply direct interaction with Na^+.

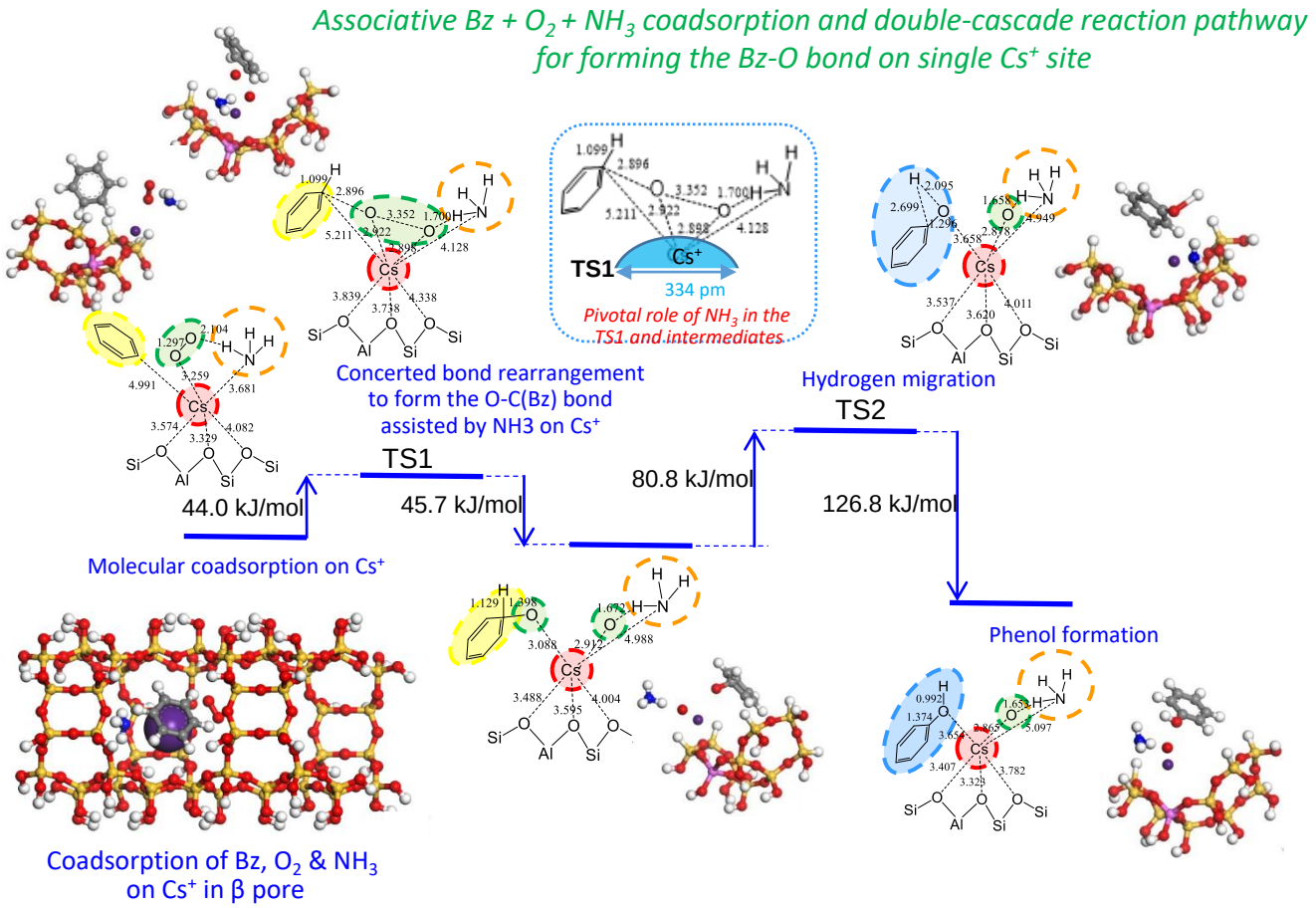
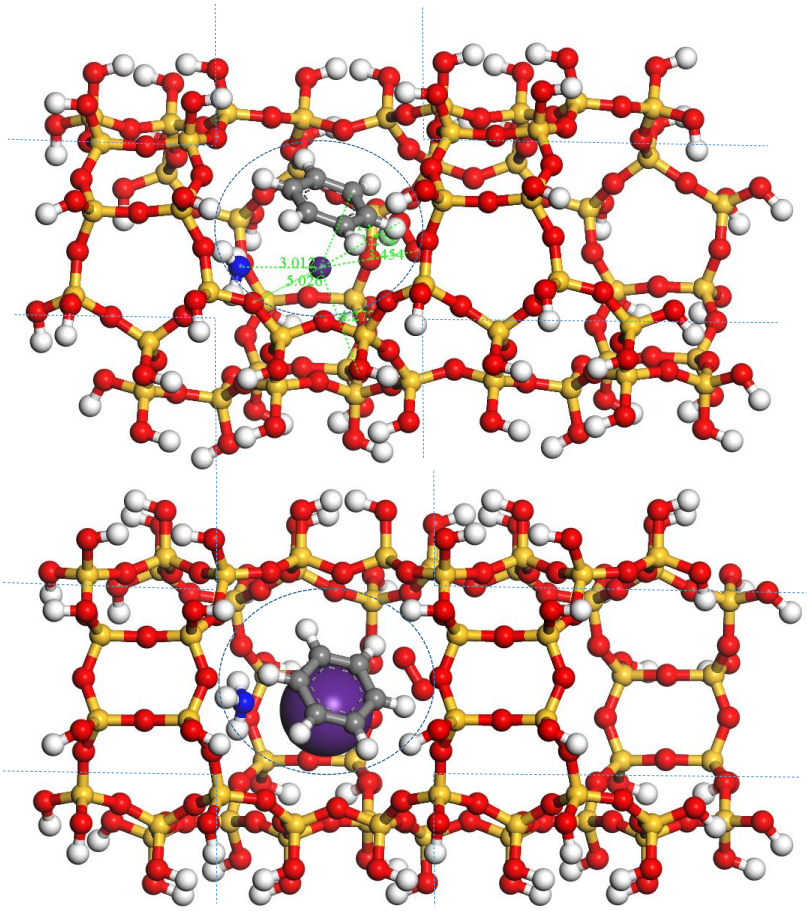


Figure S7. A computational reaction profile for the concerted inter-ligand reaction mechanism involving coadsorption states and transition states for the selective oxidation of benzene to phenol with O_2 regulated by NH_3 on the Cs^+/β cluster by DFT calculations. Cs: dark purple, O: red, C: gray, H: white, N: blue, Si: yellow, Al: pink.



Cs-N(NH_3) 0.3012 nm
Cs-O(O_2) 0.3278 nm,
0.3454 nm
O-O 0.1282 nm
Cs-C(benzene) 0.3513 nm

Figure S8. Computanional coadsorption arrangement on a Cs^+ ion incoorporated in β pore for benzene, O_2 and NH_3 by DFT calculations. Cs^+ ion has a large ion diameter of 0.334 nm, which provides a reaction platform.

Table S2. Performances (conversion and selectivity) of various transition and precious metal ions/β zeolite catalysts for the selective oxidation of benzene to phenol with O_2+NH_3 at 593 K [†]

Catalyst	Benzene conv./%	Phenol selec./%	TOF/h^{-1}	$NH_3]_{reacted}$/ $[Phenol]_{produced}$
V (2 wt%)/β	1.0	6.85	0.125	1450
Cr (2 wt%)/β	1.64	3.4	0.204	1050
Mn (2 wt%)/β	2.1	0.5	0.260	12400
Fe (2 wt%)/β	0.83	10.6	0.0704	124
Co (2 wt%)/β	0.1	35.8	0.0122	1610
Ni (2 wt%)/β	4.9	1.83	0.414	1420
Cu (2 wt%)/β	0.4	4.33	0.052	3410
Ir (2 wt%)/β	1.01	30.3	0.125	428
Ag (2 wt%)/β	0.14	54.7	0.018	992

[†] The catalysts were pretreated with benzene/O_2/NH_3/He=0.5/0.5/1.8/4 mL min^{-1} at 673 K for 0.5 h. Cat. = 0.6 g; Performance values: averaged during 30-180 min time-on-stream. Benzene/O_2/NH_3/He = 0.5/0.5/1.8/4.0 mL min^{-1}. $[NH_3]_{reacted}/[Phenol]_{produced}$: reacted NH_3 amount/produced phenol amount. TOF is defined as reacted benzene(mol)/total metal(mol)/h. Zeolite β was purchased from JGC C&C.