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Supplementary Information

Theoretical study on nitrobenzene hydrogenation to aniline catalyzed by $M_1/CeO_{2-x}(111)$ single-atom catalysts

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Table S1 Atomic radius (r_M), average M-O bond length (d_{M-O}), Bader charge (q_M), magnetic moment (Mag_M), *d*-band center (εd_{M}) of doped metal atoms in $M_1/CeO_2(111)$ and $M_1/CeO_{2-x}(111)$ surfaces, the binding energies (E_b), the cohesive energies (E_{coh}) and the oxygen vacancy formation energies (E_{ov}) of $M_1/CeO_2(111)$ surfaces. S7

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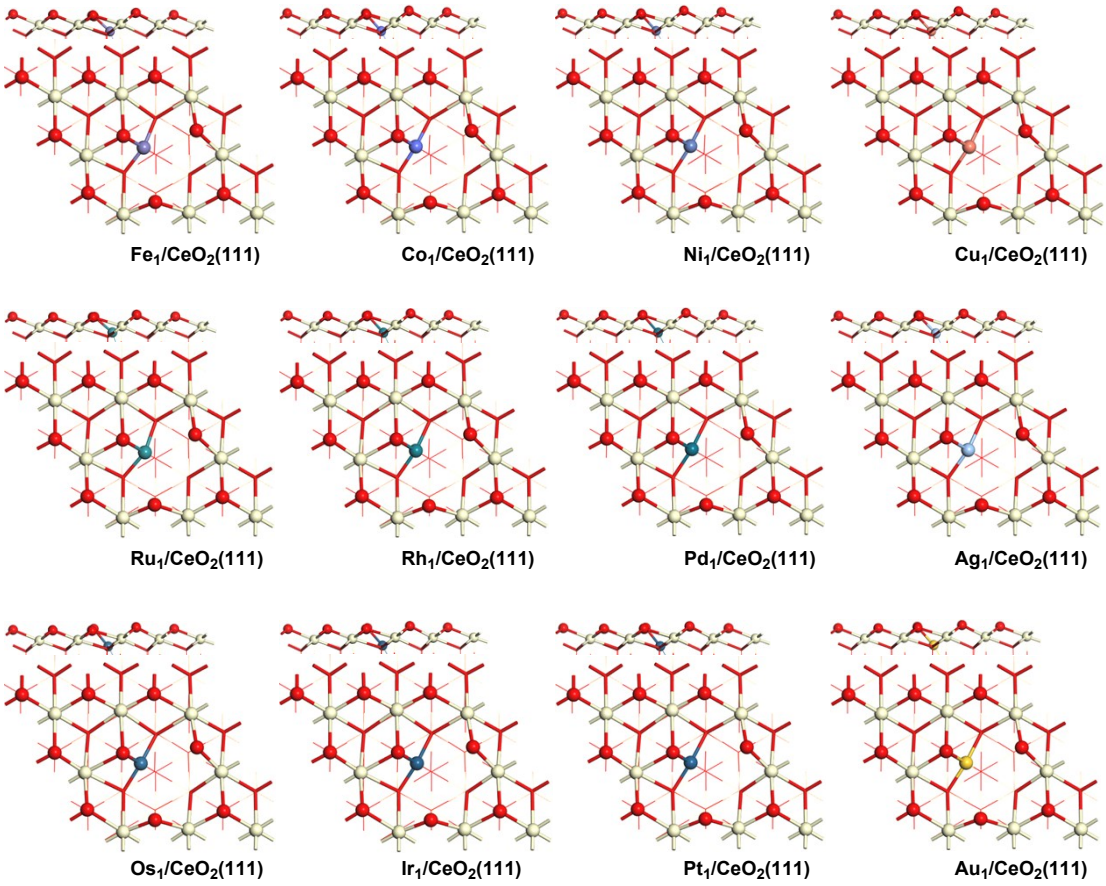

Fig. S1 The side and top view structures of $M_1/CeO_2(111)$ surfaces.

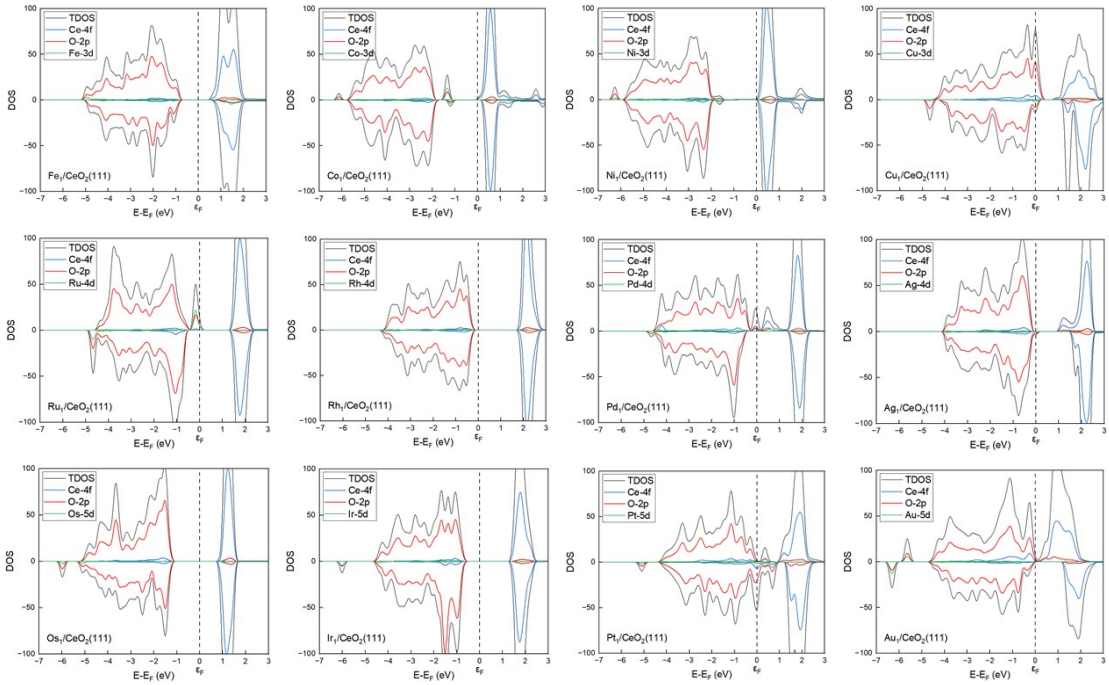

Fig. S2 Density of states (DOS) of $M_1/CeO_2(111)$ surfaces.

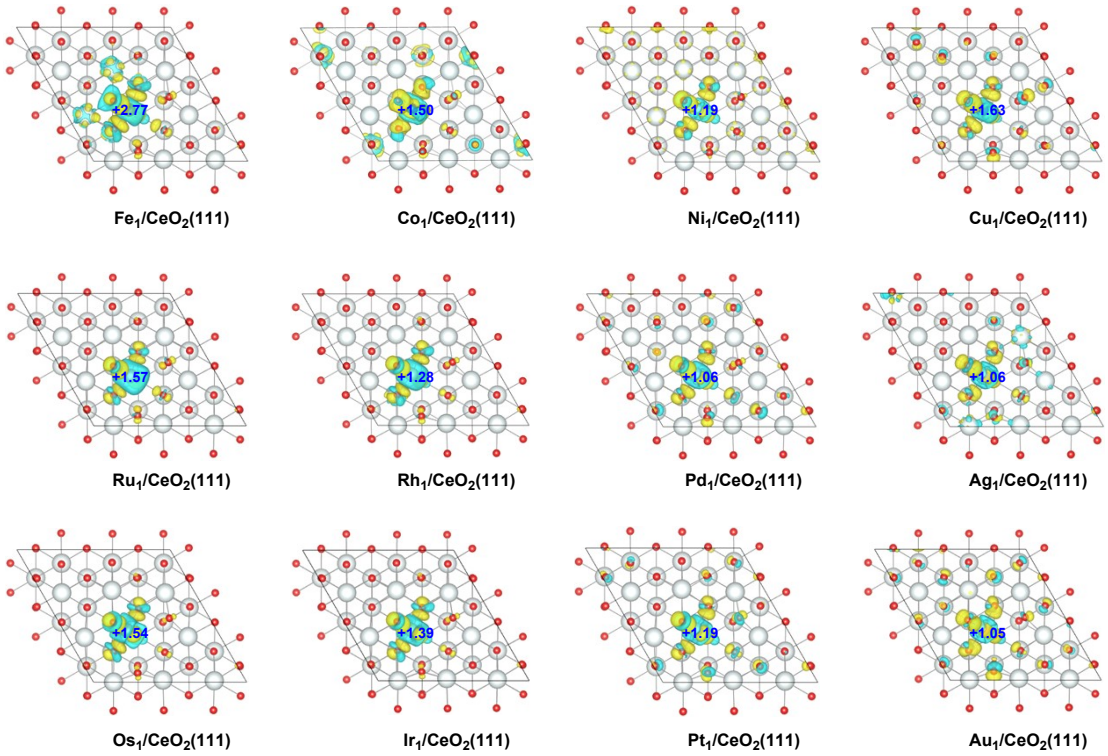

Fig. S3 Charge density difference of $M_1/CeO_2(111)$ surfaces, the data in the figure are the Bader charges (q_M) of the doped metals, with the unit |e| (the isosurface value was set to be 0.005 e/Å).

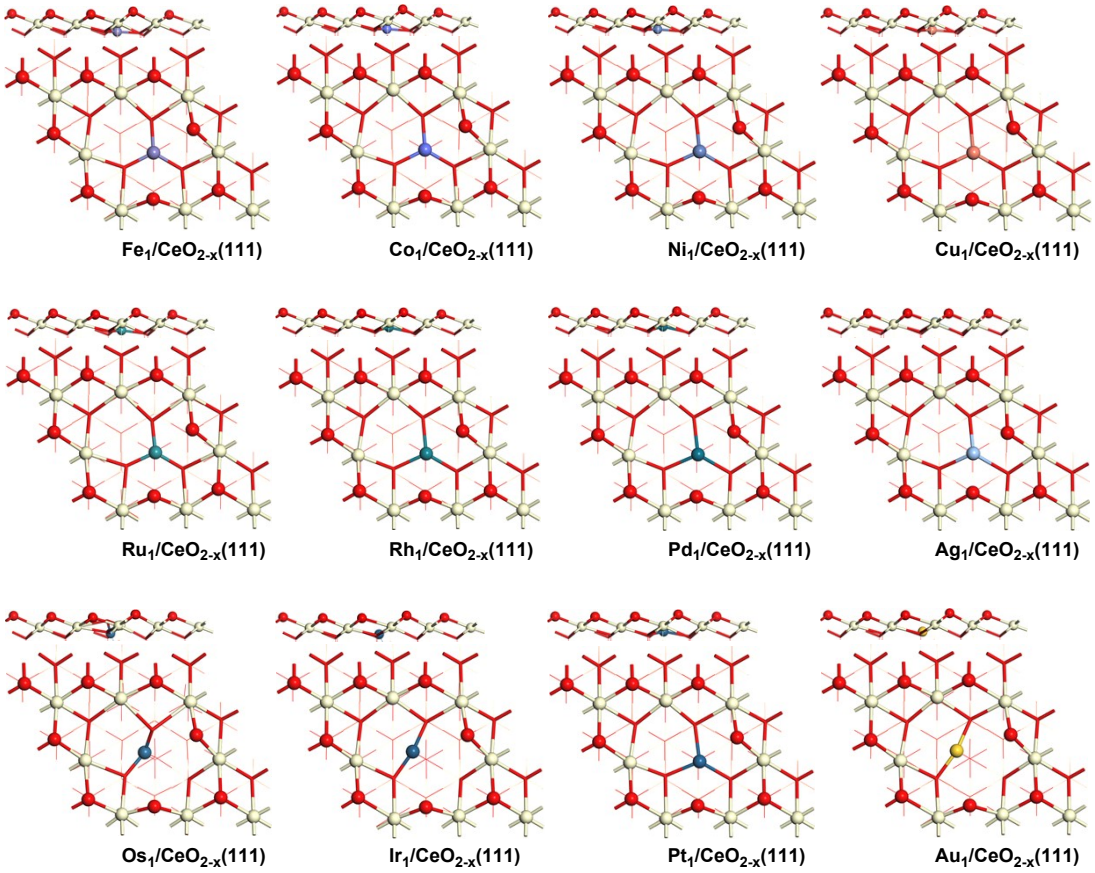

Fig. S4 The side and top view structures of $M_1/CeO_{2-x}(111)$ surfaces.

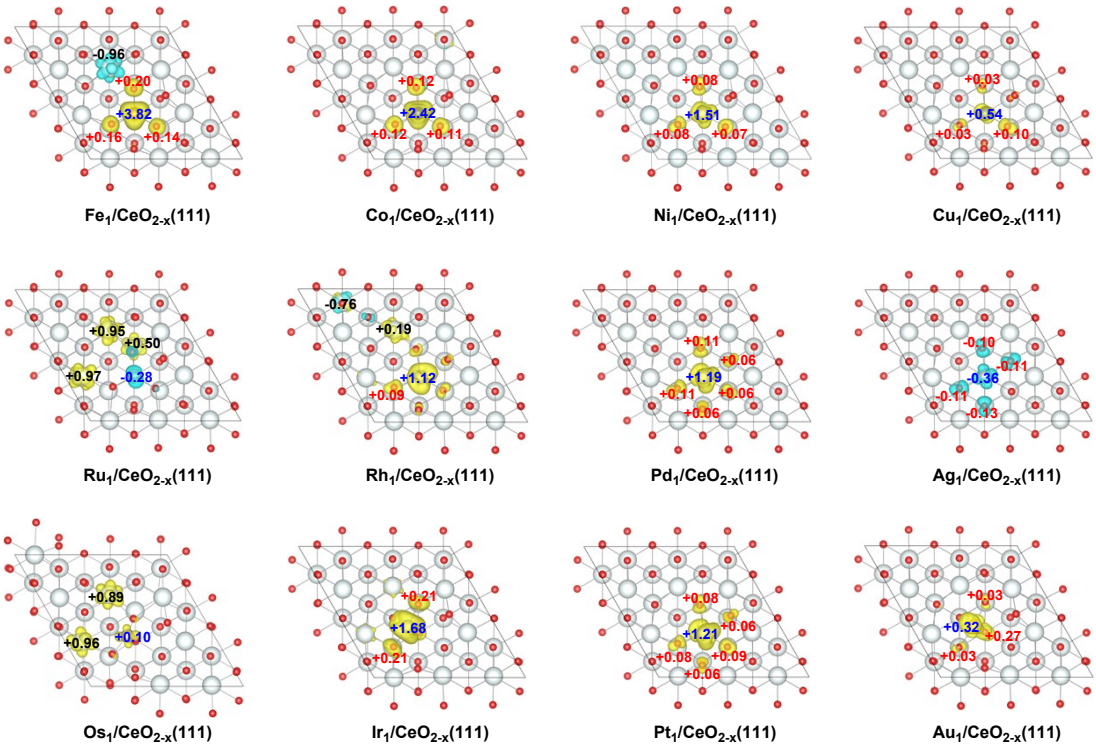

Fig. S5 The spin density of $M_1/CeO_{2-x}(111)$ surfaces, the data in the figure are magnetic moments, with the unit μ_B (the isosurface value was set to be 0.005 e/Å).

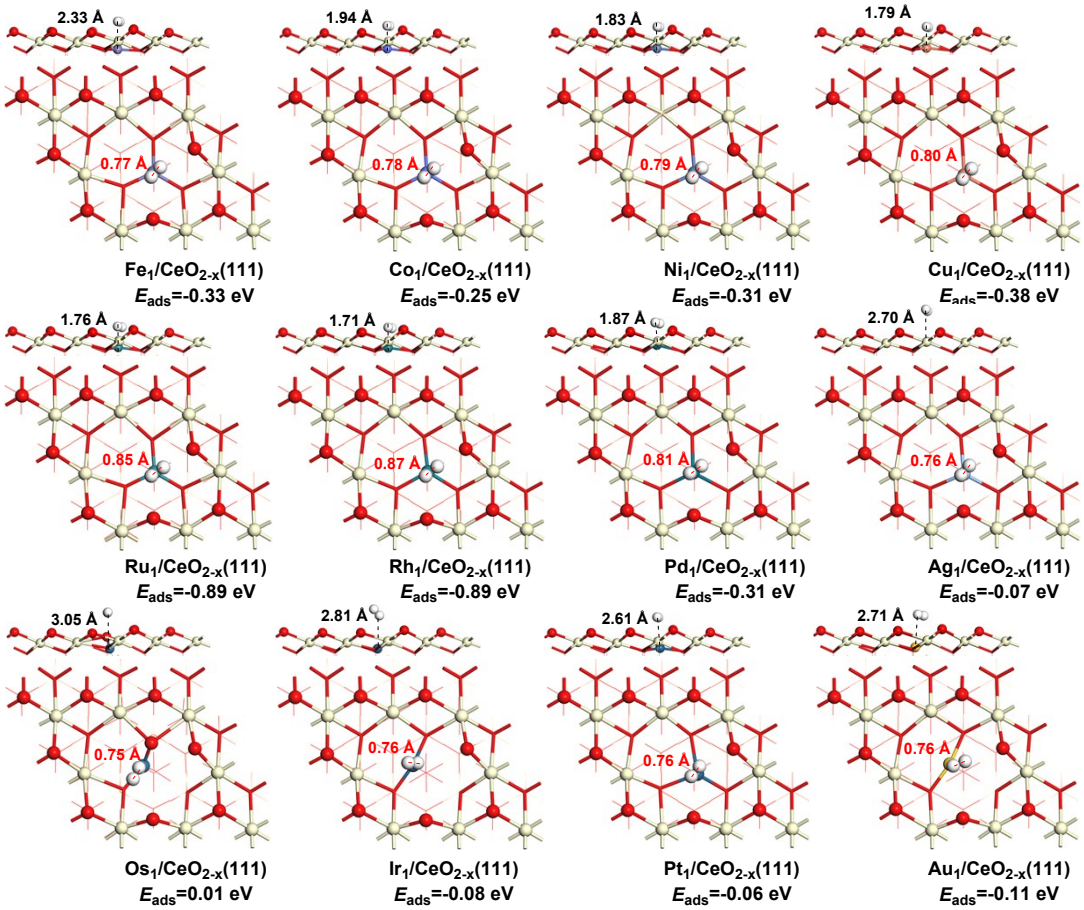

Fig. S6 The side and top view structures of H_2 adsorption on $M_1/CeO_{2-x}(111)$ surfaces.

Table S1 Atomic radius (r_M), average M-O bond length (d_{M-O}), Bader charge (q_M), magnetic moment (Mag_M), *d*-band center (εd_M) of doped metal atoms in $M_1/CeO_2(111)$ and $M_1/CeO_{2-x}(111)$ surfaces, the binding energies (E_b), the cohesive energies (E_{coh}) and the oxygen vacancy formation energies (E_{ov}) of $M_1/CeO_2(111)$ surfaces.

		$M_1/CeO_2(111)$						$M_1/CeO_{2-x}(111)$				
M	r_M (Å)	$\boldsymbol{d}_{M-O}$ (Å)	q_M (|e|)	Mag_M (μ_B)	ε_{d_M} (eV)	E_b (eV)	E_{coh} (eV)	$\boldsymbol{d}_{M-O}$ (Å)	q_M (|e|)	Mag_M (μ_B)	ε_{d_M} (eV)	E_{ov} (eV)
Fe	1.24	1.83	2.77	3.24	-1.62	7.69	4.95	1.92	1.49	3.82	-3.06	1.44
Co	1.25	1.79	1.50	0.46	-2.30	7.48	4.64	1.97	1.29	2.42	-3.22	1.46
Ni	1.25	1.82	1.19	0.96	-3.14	7.16	3.27	1.99	1.12	1.51	-2.40	0.88
Cu	1.28	1.86	1.63	0.15	-5.70	6.09	2.23	2.03	1.04	0.54	-2.46	0.63
Ru	1.33	1.94	1.57	2.64	-2.12	7.69	6.68	1.89	1.65	-0.28	-5.03	1.79
Rh	1.35	1.91	1.28	1.62	-3.36	7.33	4.05	2.16	1.18	1.12	-3.92	2.14
Pd	1.38	1.95	1.06	0.70	-2.68	5.89	2.25	2.21	0.89	1.19	-3.10	1.10
Ag	1.44	2.00	1.06	-0.01	-2.48	4.65	1.59	2.44	0.87	-0.36	-2.53	-0.06
Os	1.34	1.89	1.54	1.30	-5.80	9.18	4.93	2.11	1.31	0.10	-4.87	3.16
Ir	1.36	1.91	1.39	1.65	-4.45	9.59	3.39	2.27	0.77	1.68	-1.93	3.25
Pt	1.39	1.93	1.19	0.80	-1.51	8.82	1.66	2.17	0.89	1.21	-3.90	2.67
Au	1.44	1.99	1.05	0.04	-4.86	6.49	0.61	2.34	0.62	0.32	-2.26	1.22

Note S1 The thermodynamics of the uncatalyzed reaction.

It is important to present the thermodynamics of the uncatalyzed reaction, especially for the conversion of $PhNO_2$ to PhNO, then to PhNHOH, and further to $PhNH_2$. The relevant thermodynamic equations and Gibbs free energy changes (ΔG) for each step are listed below:

1. $PhNO_2$ to PhNO:

$$PhNO_2 + H_2 \rightarrow PhNO + H_2O$$

$$\Delta G_1 = G_{(PhNO)} + G_{(H2O)} - G_{(PhNO2)} - G_{(H2)} = -83.46 + (-14.14) - (-89.93) - (-6.66) = -1.01 \text{ eV}$$

2. PhNO to PhNHOH:

$$PhNO + H_2 \rightarrow PhNHOH$$

$$\Delta G_2 = G_{(PhNHOH)} - G_{(PhNO)} - G_{(H2)} = -91.16 - (-83.46) - (-6.66) = -1.05 \text{ eV}$$

3. PhNHOH to $PhNH_2$:

$$PhNHOH + H_2 \rightarrow PhNH_2 + H_2O$$

$$\Delta G_3 = G_{(PhNH2)} + G_{(H2O)} - G_{(PhNHOH)} - G_{(H2)} = -86.21 + (-14.14) - (-91.16) - (-6.66) = -2.54 \text{ eV}$$

4. Overall reaction ($PhNO_2$ to $PhNH_2$):

$$PhNO_2 + 3H_2 \rightarrow PhNH_2 + 2H_2O$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = G_{(PhNH2)} + 2G_{(H2O)} - G_{(PhNO2)} - 3G_{(H2)} = -86.21 + 2*(-14.14) - (-89.93) - 3*(-6.66) = -4.60 \text{ eV}$$

Therefore, the uncatalyzed reaction of $PhNO_2$ to PhNO, then to PhNHOH, and further to $PhNH_2$ are exothermic. Overall, the uncatalyzed reaction of $PhNO_2$ to $PhNH_2$ is also exothermic, with a total Gibbs free energy change of -4.60 eV.