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The sensing mechanism of pristine and transition metals doped $Zn_{12}O_{12}$, $Sn_{12}O_{12}$ and $Ni_{12}O_{12}$ nanocages towards NH_3 and PH_3: A DFT study

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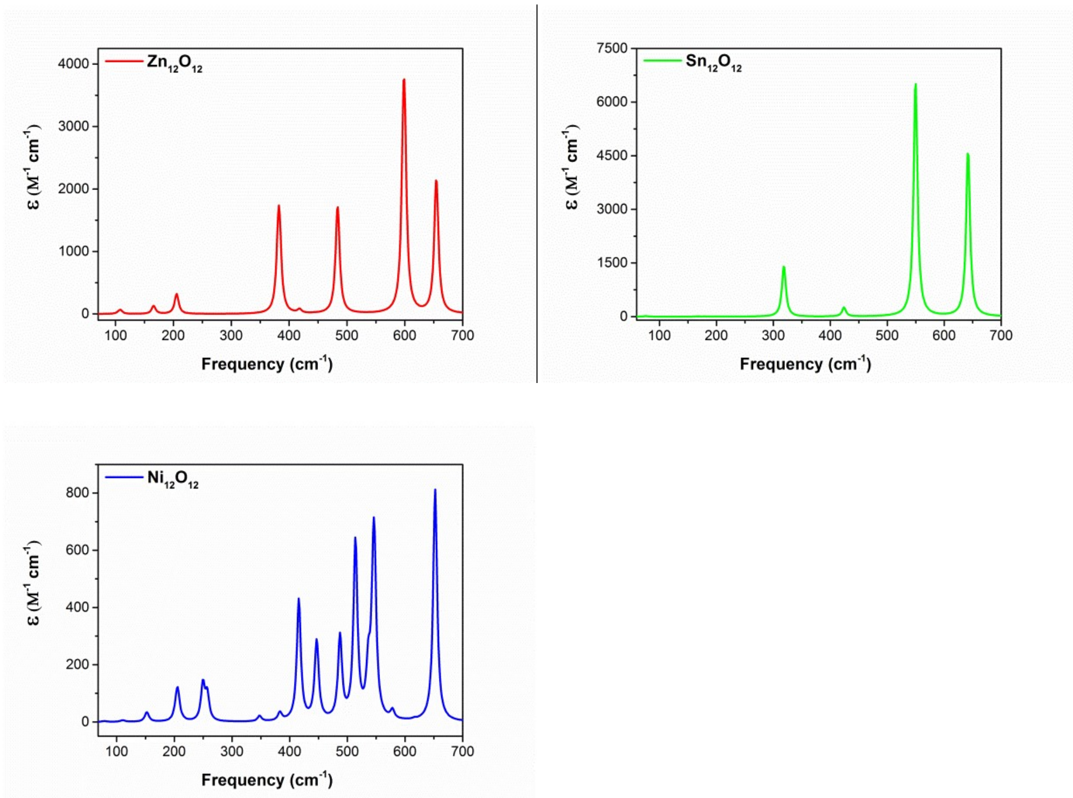

Fig. S1. Vibrational spectra of $Zn_{12}O_{12}$, $Sn_{12}O_{12}$ and $Ni_{12}O_{12}$ nanocages.

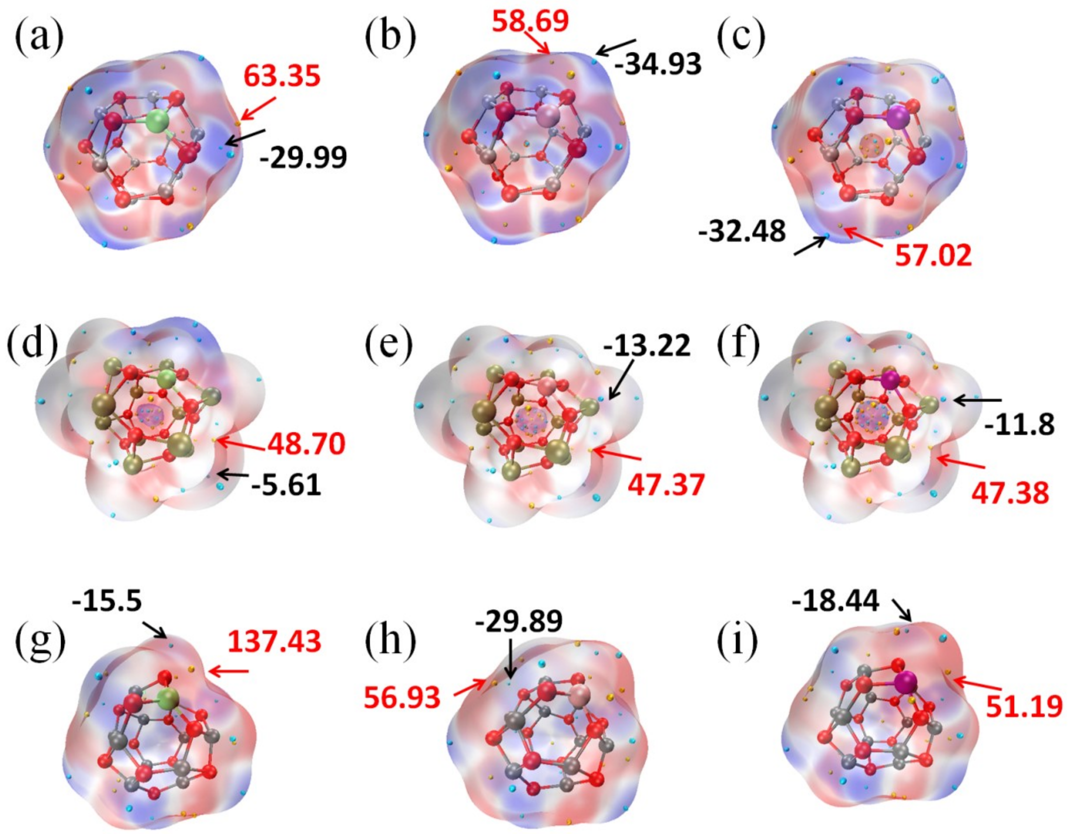

Fig. S2. ESP surfaces of (a) $Zn_{11}TiO_{12}$, (b) $Zn_{11}CrO_{12}$, (c) $Zn_{11}FeO_{12}$, (d) $Sn_{11}TiO_{12}$, (e) $Sn_{11}CrO_{12}$, (f) $Sn_{11}FeO_{12}$, (g) $Ni_{11}TiO_{12}$, (h) $Ni_{11}CrO_{12}$, and (i) $Ni_{11}FeO_{12}$, respectively.

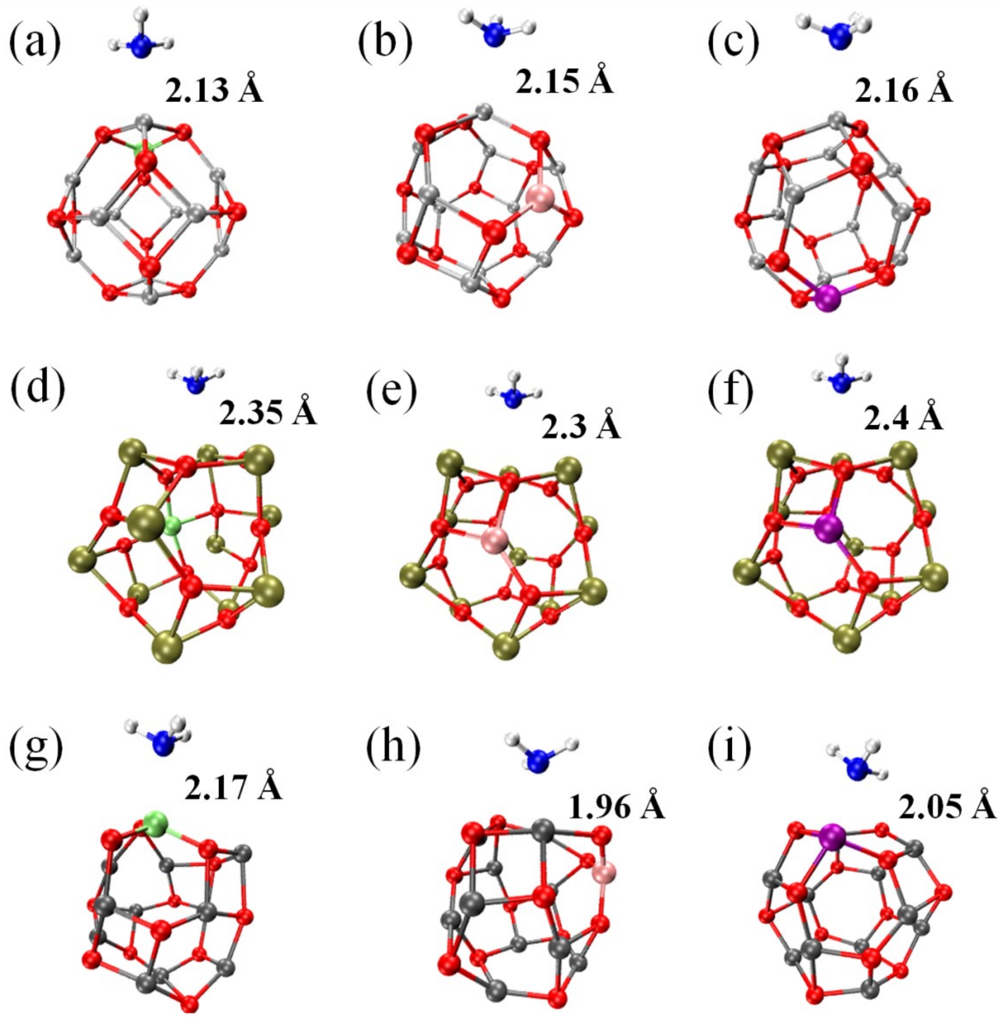

Fig. S3. The stable structures for the adsorption of NH_3 on (a) $Zn_{11}TiO_{12}$, (b) $Zn_{11}CrO_{12}$, (c) $Zn_{11}FeO_{12}$, (d) $Sn_{11}TiO_{12}$, (e) $Sn_{11}CrO_{12}$, (f) $Sn_{11}FeO_{12}$, (g) $Ni_{11}TiO_{12}$, (h) $Ni_{11}CrO_{12}$, and (i) $Ni_{11}FeO_{12}$, respectively.

Table S1 Electronic properties including energy level, energy gap, hardness (η), electronic chemical potential (μ), electrophilicity index (ω) and work function (Φ). All parameters are in eV.

	E_H	E_L	E_g	η	μ	ω	Φ	%$\Delta\Phi$	τ
$Zn_{11}TiO_{12}$	−4.19	−2.72	1.47	0.74	−3.46	8.12	3.46	-	-
$Zn_{11}TiO_{12}/NH_3$	−3.92	−2.29	1.63	0.82	−3.11	5.91	3.11	−10.12	1.2×10^{6} s
$Zn_{11}CrO_{12}$	−4.65	−2.74	1.91	0.96	−3.70	7.15	3.70	-	-
$Zn_{11}CrO_{12}/NH_3$	−4.37	−2.34	2.03	1.02	−3.36	5.54	3.36	−9.19	3.3×10^{3} s
$Zn_{11}FeO_{12}$	−5.39	−2.74	2.65	1.33	−4.07	6.24	4.07	-	-
$Zn_{11}FeO_{12}/NH_3$	−5.10	−2.34	2.76	1.38	−3.72	5.01	3.72	−8.60	0.5×10^{3} s
$Sn_{11}TiO_{12}$	−3.44	−1.76	1.68	0.84	−2.60	4.02	2.60	-	-
$Sn_{11}TiO_{12}/NH_3$	−4.35	−1.93	2.42	1.21	−3.14	4.07	3.14	20.77	1.9×10^{11} ns
$Sn_{11}CrO_{12}$	−4.94	−1.92	3.02	1.51	−3.43	3.90	3.43	-	-

$Sn_{11}CrO_{12}/NH_3$	−4.72	−1.71	3.01	1.51	−3.22	3.43	3.22	−6.12	12 ns
$Sn_{11}FeO_{12}$	−5.89	−2.15	3.74	1.87	−4.02	4.32	4.02	-	-
$Sn_{11}FeO_{12}/NH_3$	−5.69	−1.96	3.73	1.87	−3.83	3.92	3.83	−4.73	104 ns
$Ni_{11}TiO_{12}$	−6.47	−4.88	1.59	0.80	−5.68	20.26	5.68	-	-
$Ni_{11}TiO_{12}/NH_3$	−5.67	−4.09	1.58	0.79	−4.88	15.07	4.88	−14.08	3.5×10^{17} s
$Ni_{11}CrO_{12}$	−6.45	−5.06	1.39	0.70	−5.76	23.83	5.76	-	-
$Ni_{11}CrO_{12}/NH_3$	−6.18	−4.68	1.50	0.75	−5.43	19.66	5.43	−5.73	2.4×10^{2} s
$Ni_{11}FeO_{12}$	−6.65	−4.74	1.91	0.96	−5.70	16.98	5.70	-	-
$Ni_{11}FeO_{12}/NH_3$	−6.27	−4.40	1.87	0.94	−5.34	15.22	5.34	−6.32	6.9×10^{8} s