Supplementary Information

How Spin State and Oxidation Number of Transition Metal Atoms Determine Molecular Adsorption: A First-Principles Case Study for NH_3

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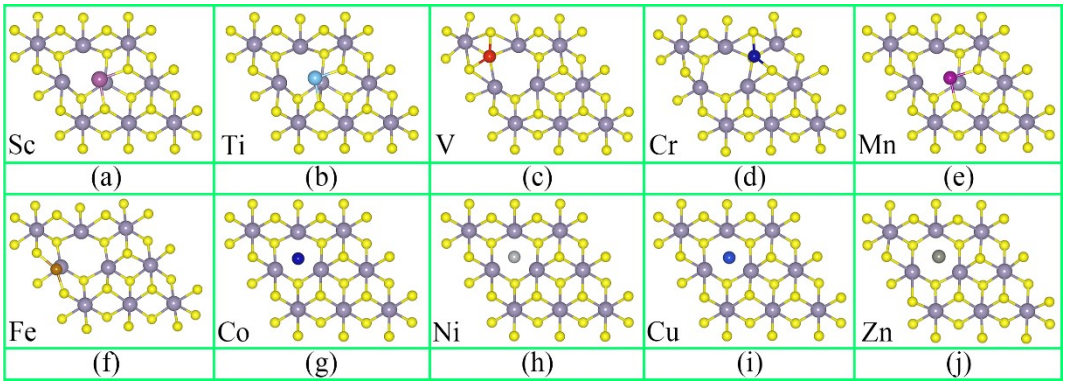

Fig. S1. *The top views of optimized TM@S_v-SnS_2 structures, with Sc~Zn atoms correspond to (a)-(j), respectively.*

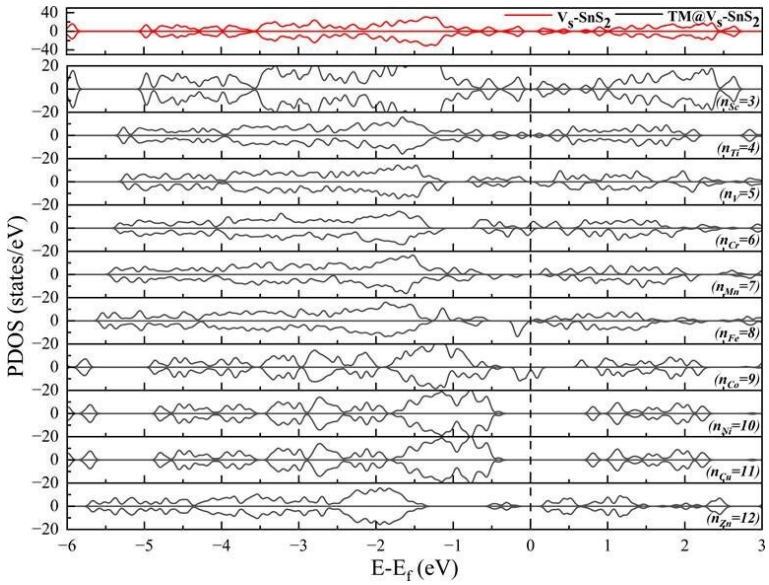

Fig. S2. *The total electronic density of states for the substrates of TM@S_v-SnS_2 without TM atoms in different electron number n, together with case of S_v-SnS_2 for comparison.*

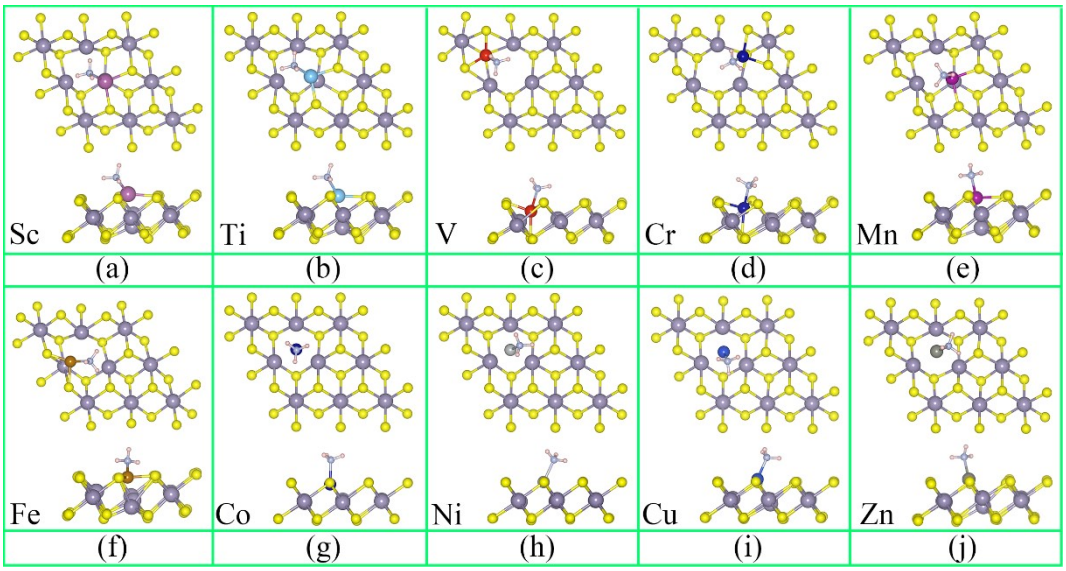

Fig. S3. *The upper/lower part corresponds to the top/side views of NH_3 adsorbed at TM@S_v-SnS_2 surfaces, with Sc~Zn correspond to (a)-(j). The N and H atoms are in silver white and pink, respectively.*

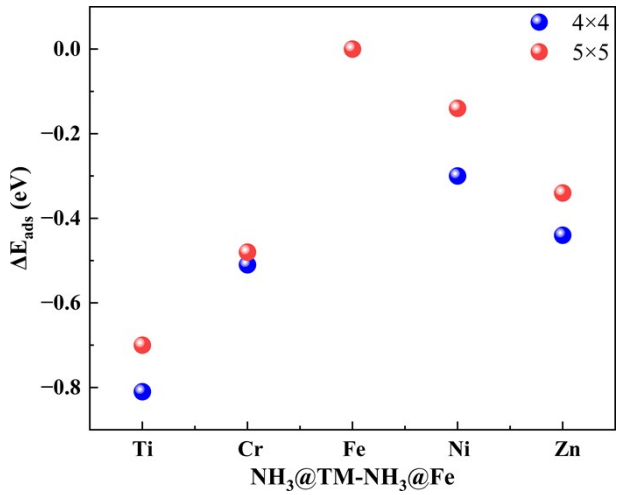

Fig. S4. *The size effect of supercell on the NH_3 adsorption at TM@S_v-SnS_2 in different even electron number n. For clear, the highest values for both (4×4) and (5×5) cases are set to zero.*

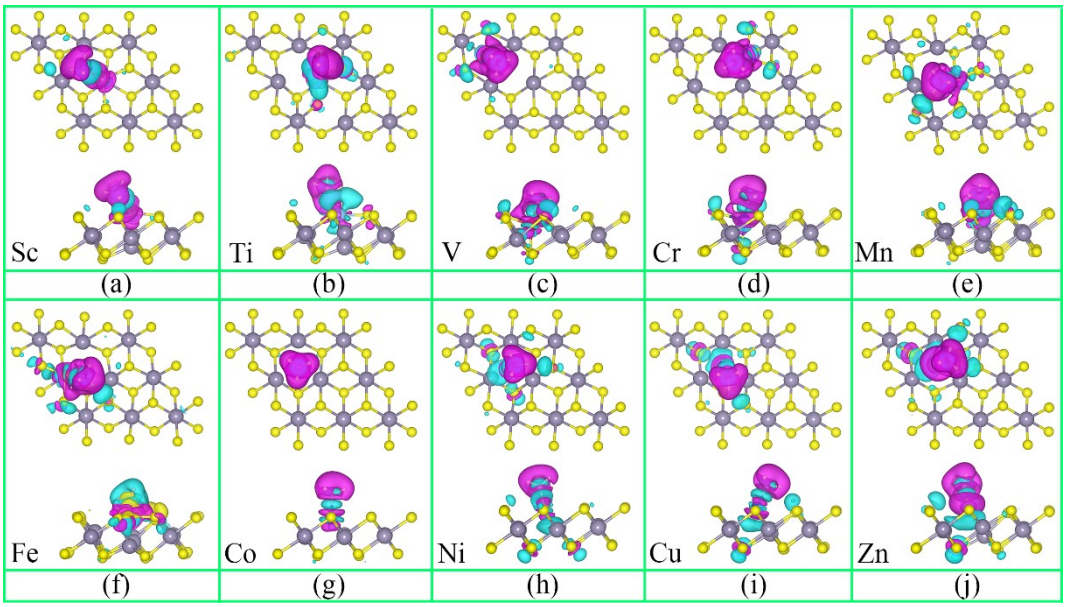

Fig. S5. *The top and side views of charge density difference of NH_3@TM@ S_v-SnS_2 structures, with Sc~Zn correspond to (a)-(j), respectively. The purple and cyan areas indicate electron depletion and accumulation, with an isosurface of 10^{-3} e/Å^3.*

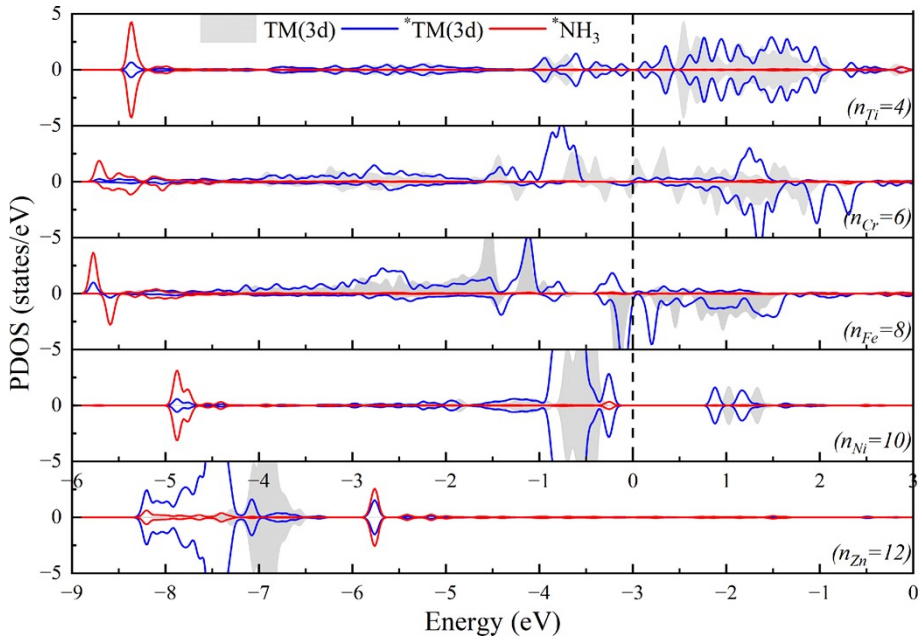

Fig. S6. *The DOS of NH_3@TM@S_v-SnS_2 with TM atoms in even electron number n. Star * denotes NH_3 adsorbed at surface.*

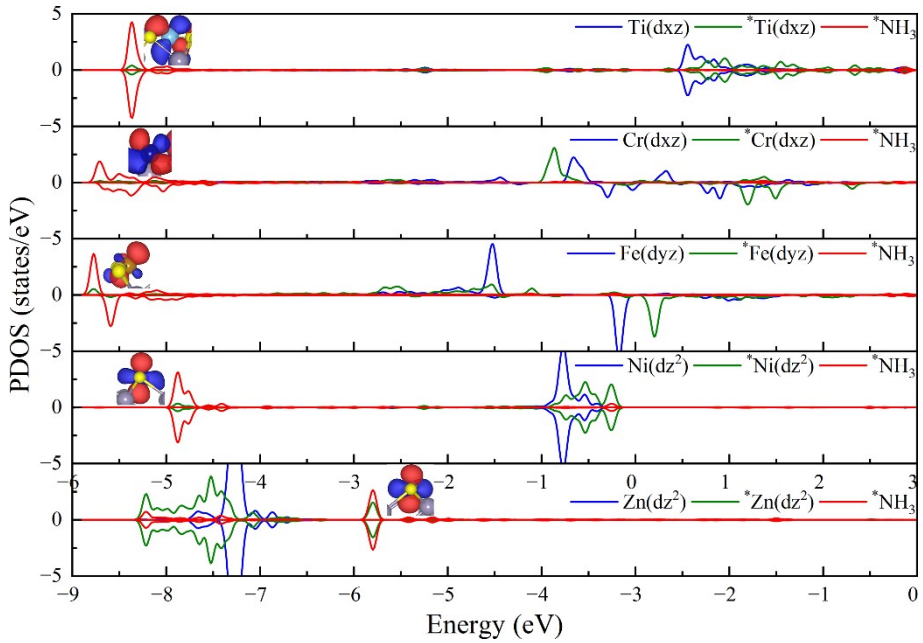

Fig. S7. *The projected DOS of 3d orbital as well as 3σ orbital of adsorbed NH_3 for TM atoms in even electron number n. The corresponding interacted orbitals are also provided in the inset, with an isosurface of 10^{-7} e/Å^3, respectively.*

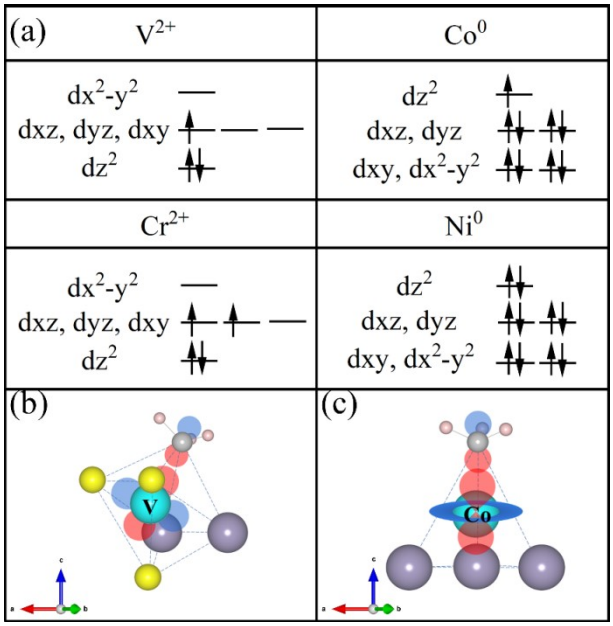

Fig. S8. *(Color online) (a) The illustration of outermost valence electron filling in the 3d orbitals of TM ions in TM@S_v-Sn for V^{2+}, Cr^{2+}, Co^0, and Ni^0 ions. The corresponding frontier orbitals between 3σ of NH_3 and 3d orbital of TM ions with (b) dxz orbital, and (c) dz^2 orbital, respectively.*