Supplementary Information
Pristine and ruthenium-doped TiO_2 nanoclusters for nitrogen fixation: First-principles modeling of structure and adsorption

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1. Optimized structures

1.1. $(TiO_2)_n$ clusters

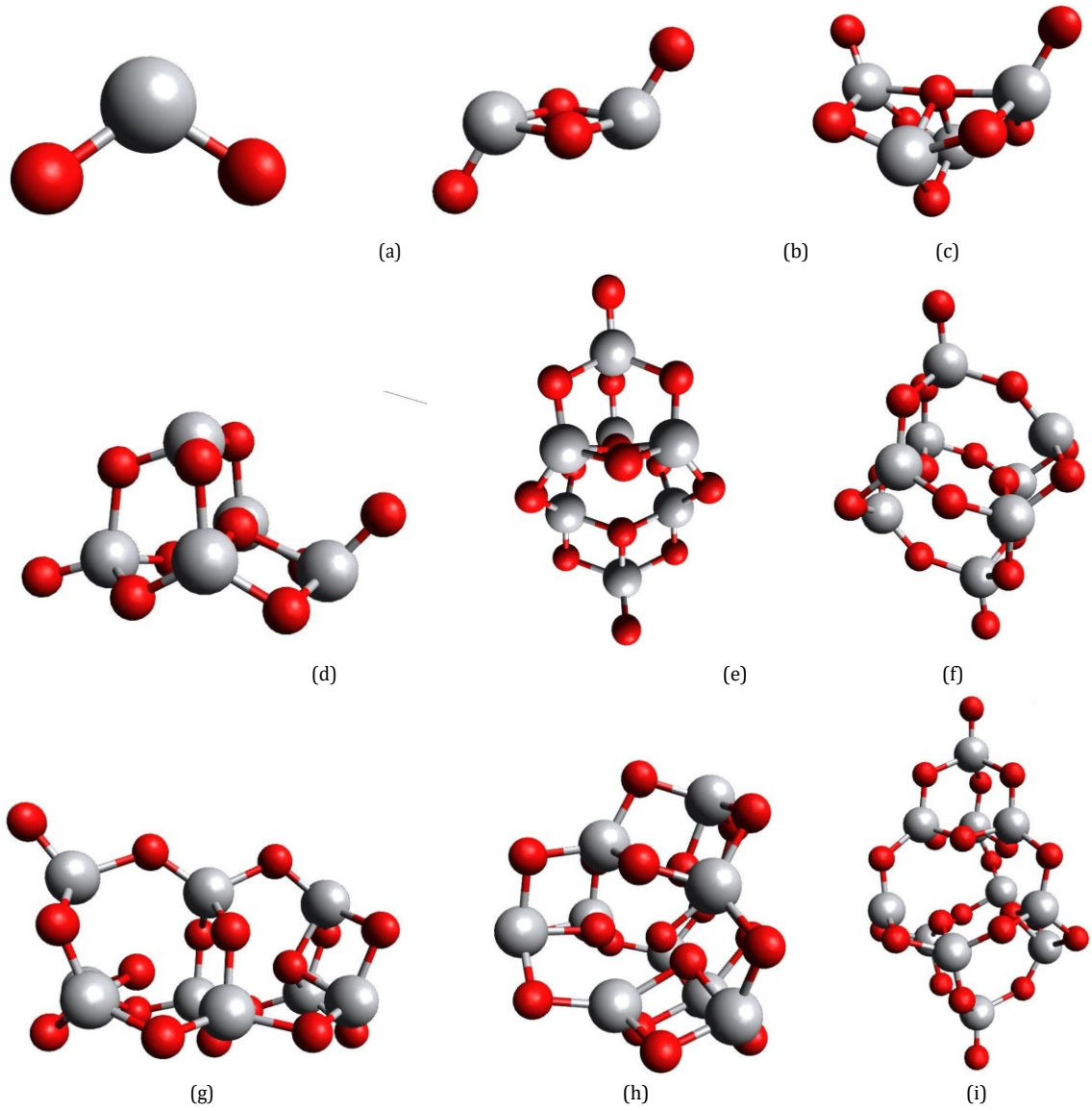
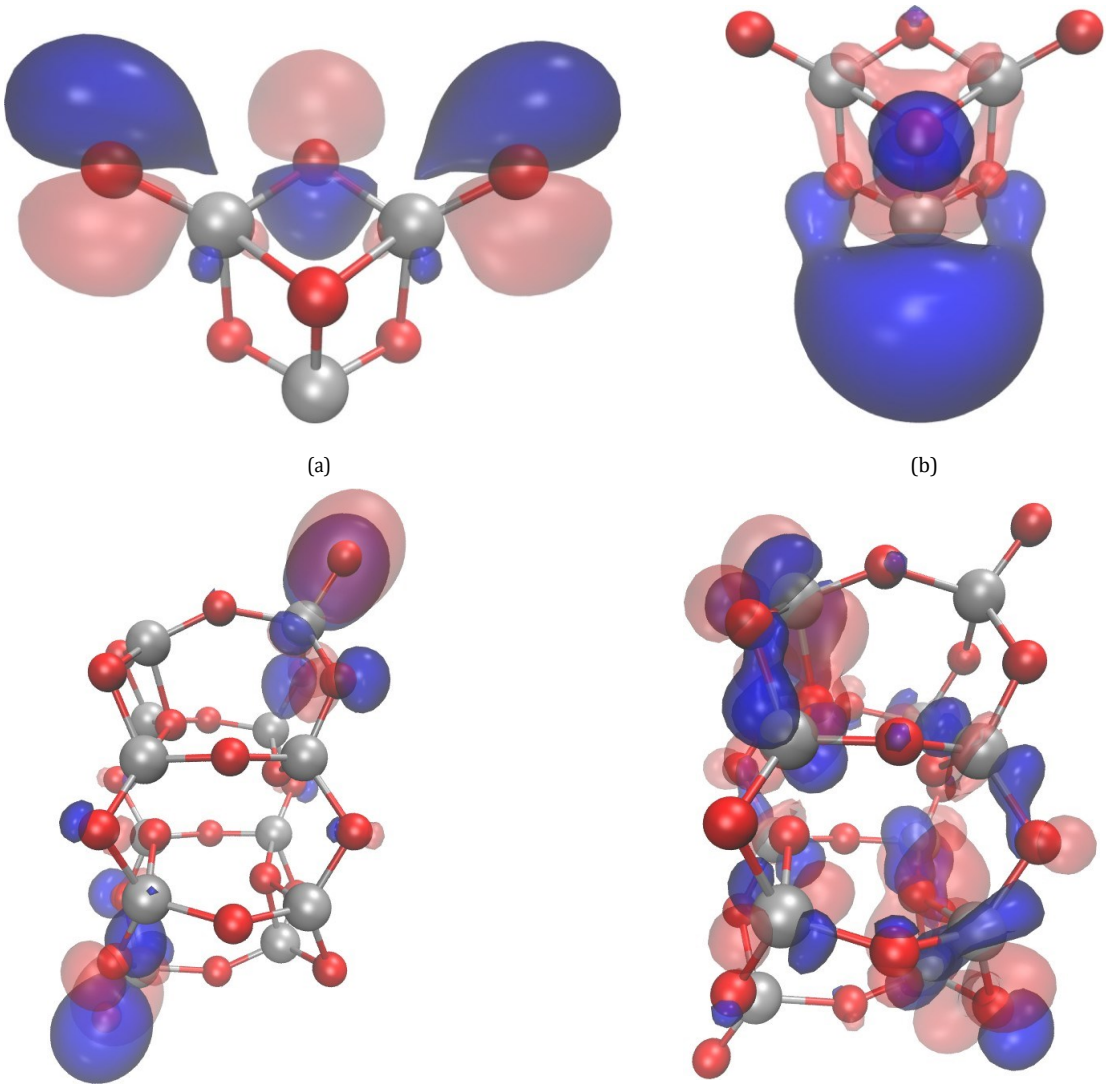


Figure S1: Optimized structures of a) $(TiO_2)_1$, b) $(TiO_2)_2$, c) $(TiO_2)_4$, d) $(TiO_2)_5$, e) $(TiO_2)_7$, f) $(TiO_2)_8$, g) $(TiO_2)_9$, h) $(TiO_2)_{10}$, i) $(TiO_2)_{11}$

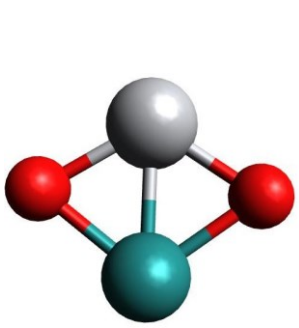


(a) (b)

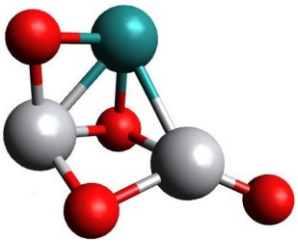
(c) (d)

Figure S2: HOMO and LUMO orbitals of TiO_2 clusters at an isovalue of $\pm$ 0.02 $e_0/Å^3$. a) HOMO of $(TiO_2)_3$ b) LUMO of $(TiO_2)_3$ c) HOMO of $(TiO_2)_{12}$ d) LUMO of $(TiO_2)_{12}$.

1.2. Ru-$(TiO_2)_n$ clusters



(a)



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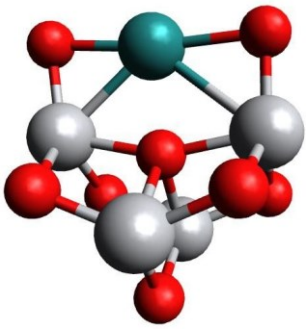

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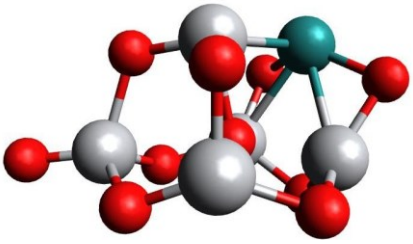

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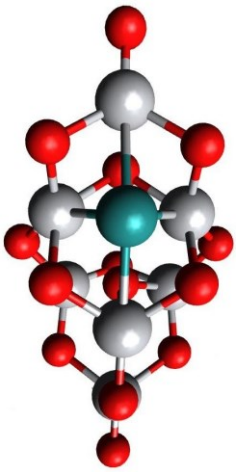

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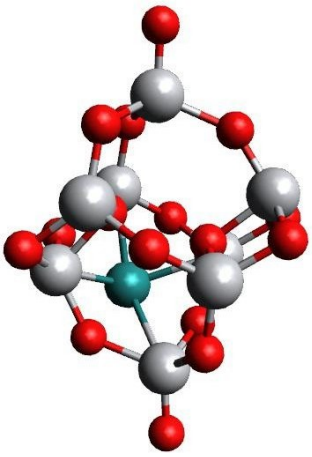
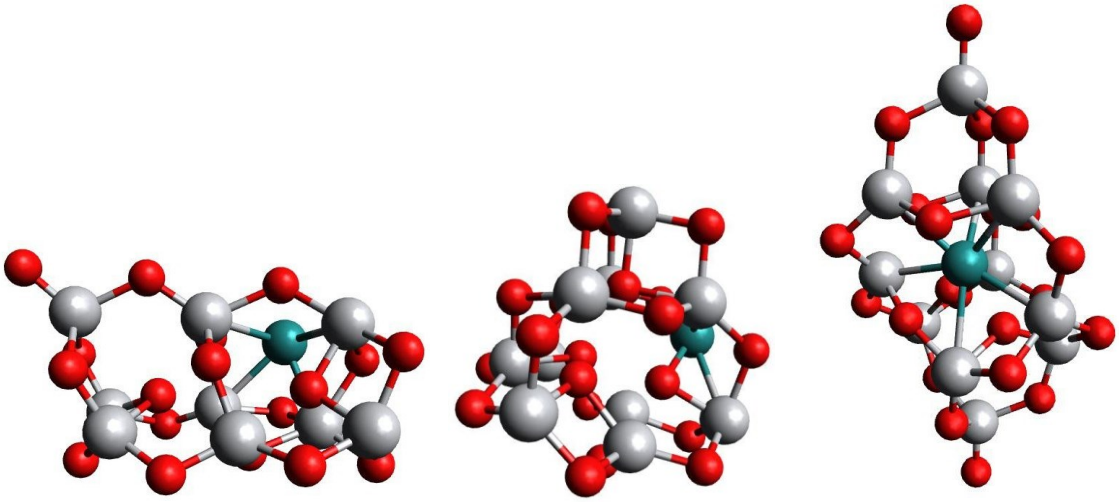
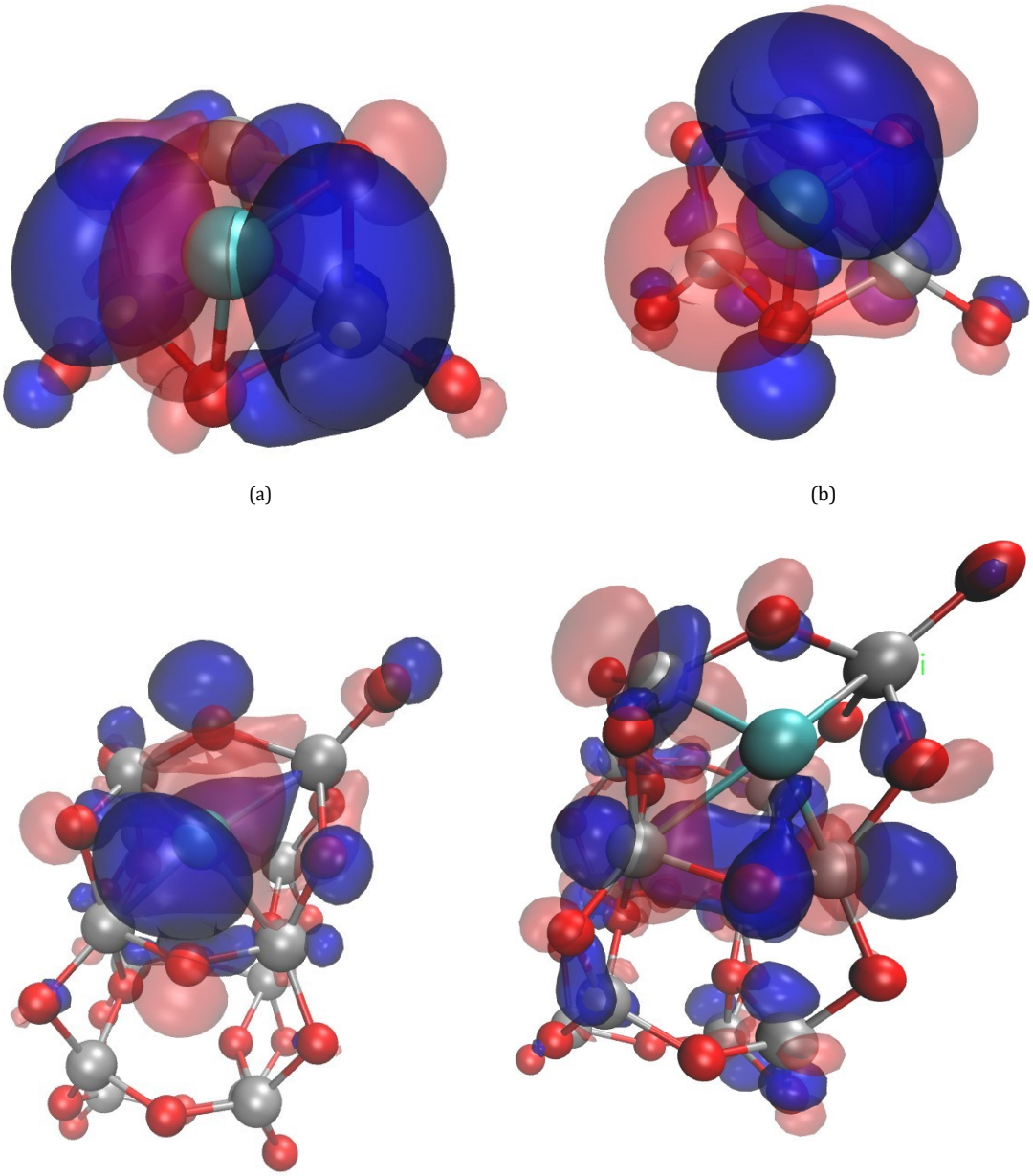


(f)



(g) (h) (i)

Figure S3: Optimized structures of a) Ru-$(TiO_2)_1$, b) Ru-$(TiO_2)_2$, c) Ru-$(TiO_2)_4$, d) Ru-$(TiO_2)_5$, e) Ru-$(TiO_2)_7$, f) Ru-$(TiO_2)_8$, g) Ru-$(TiO_2)_9$, h) Ru-$(TiO_2)_{10}$, i) Ru-$(TiO_2)_{11}$.



(a) (b)

(c) (d)

Figure S4: HOMO and LUMO orbitals of Ru-TiO_2 clusters at an isovalue of $\pm$ 0.02 $e_0/Å^3$. a) HOMO of Ru-$(TiO_2)_3$ b) LUMO of Ru-$(TiO_2)_3$ c) HOMO of Ru-$(TiO_2)_{12}$ d) LUMO of Ru-$(TiO_2)_{12}$.

2. Electronic properties

2.1. $((TiO_2)_n$ clusters

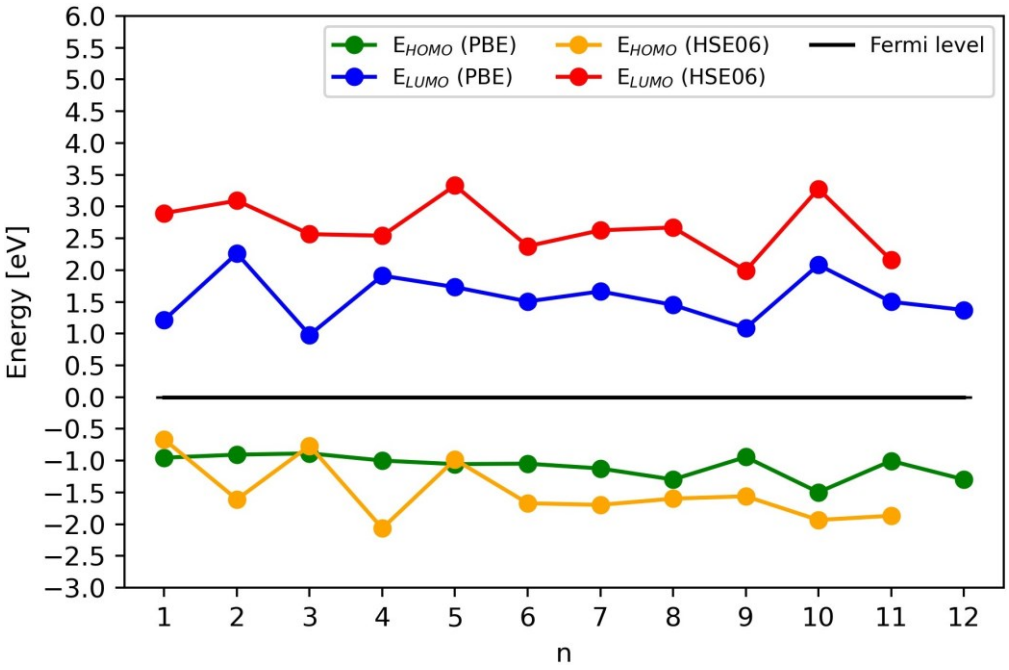
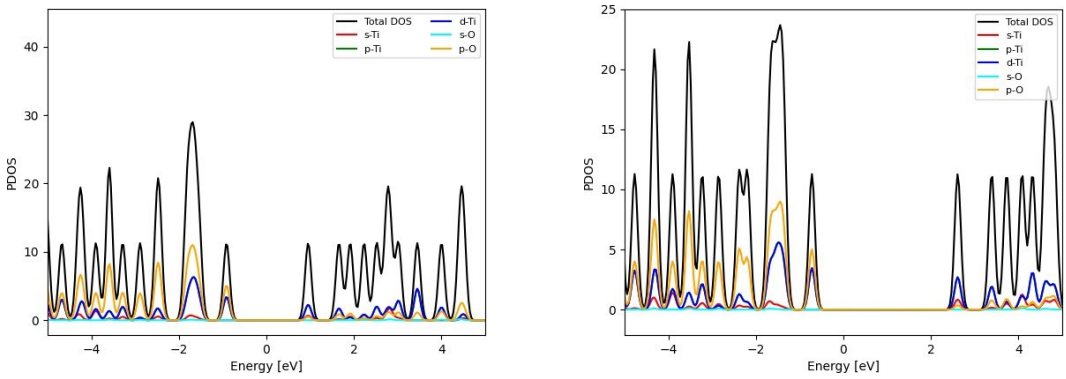


Figure S5: HOMO and LUMO positions relative to the Fermi level (0.0 eV) of TiO_2 clusters calculated with PBE and HSE06 functionals.



(a) PBE functional

(b) HSE functional

Figure S6: Total density of states and projected density of states of the $(TiO_2)_3$ cluster calculated with PBE and HSE06 functionals.

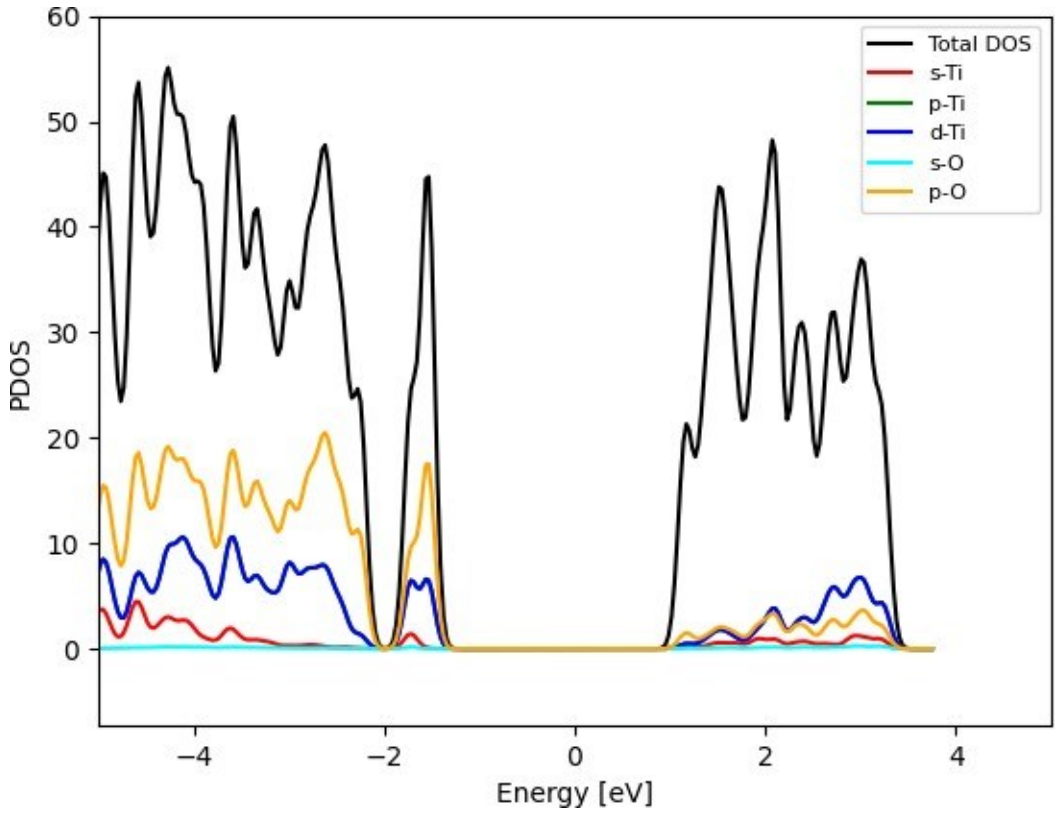


Figure S7: Total density of states and projected density of states of the $(TiO_2)_{12}$ cluster calculated with the PBE functional.

2.2. *Ru-$(TiO_2)_n$ clusters*

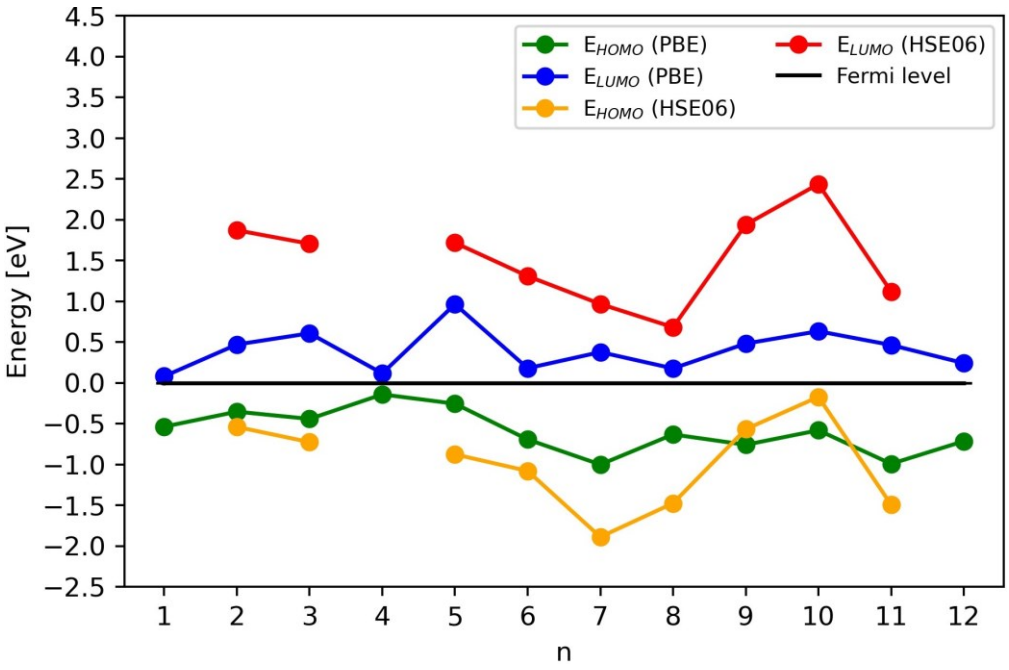
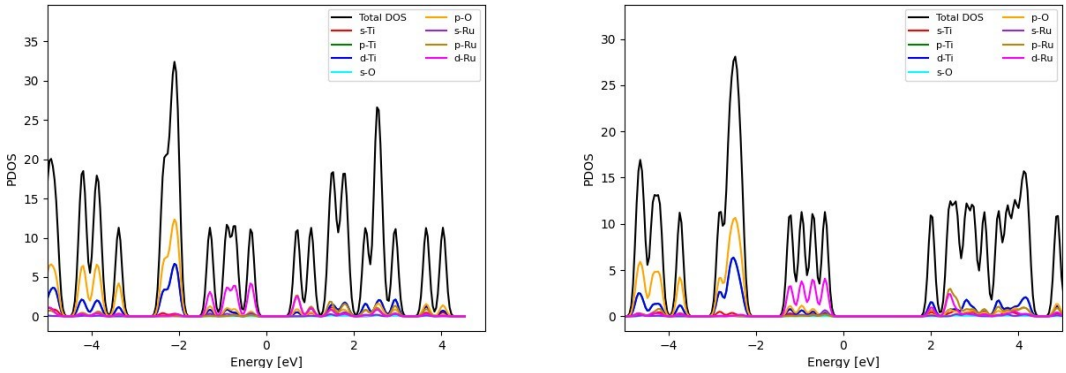


Figure S8: HOMO and LUMO positions relative to the Fermi level (0.0 eV) of Ru-TiO_2 clusters calculated with PBE and HSE06 functionals.



(a) PBE functional

(b) HSE functional

Figure S9: Total density of states and projected density of states of the Ru-$(TiO_2)_3$ cluster calculated with PBE and HSE06 functionals.

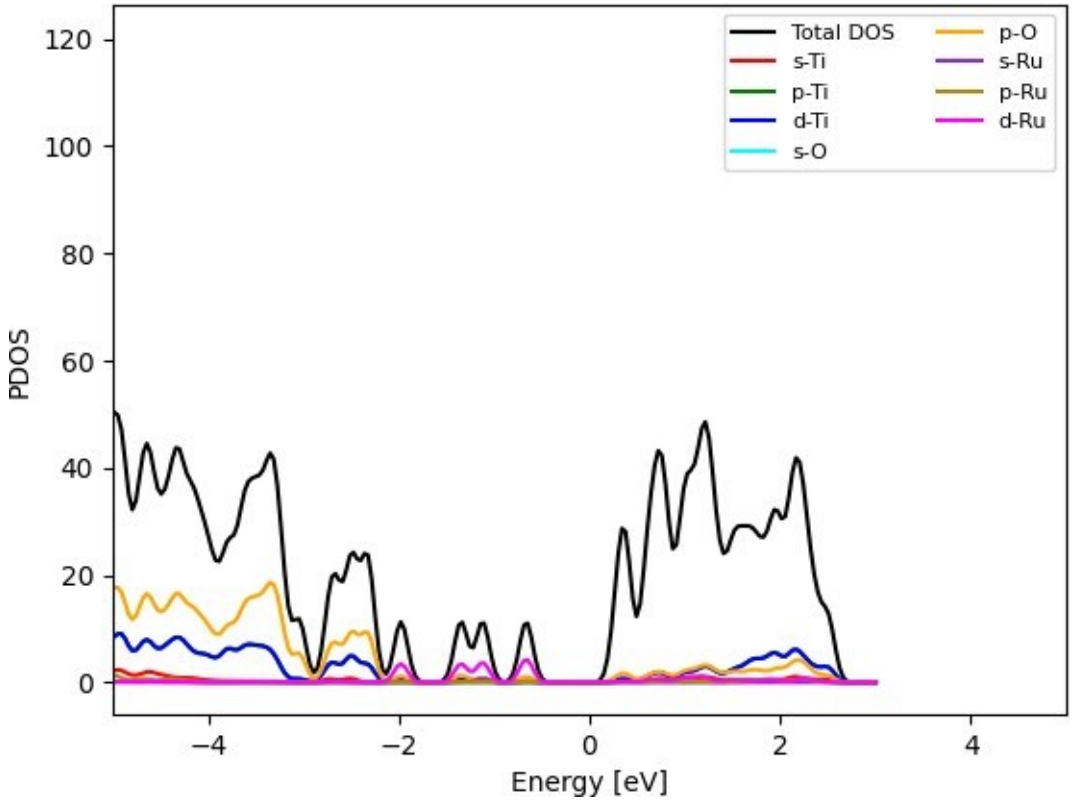
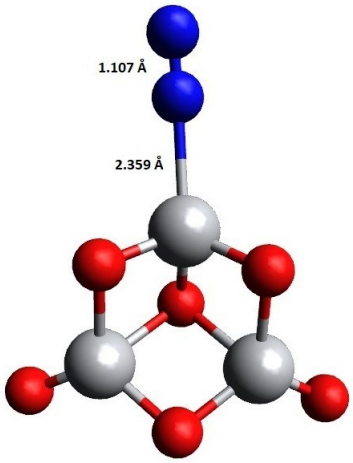


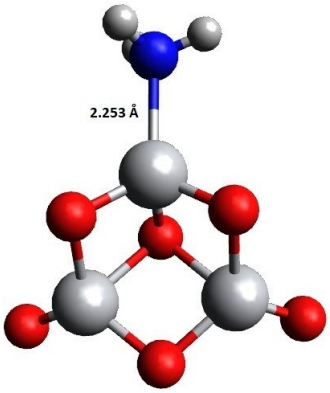
Figure S10: Total density of states and projected density of states of the Ru-$(TiO_2)_{12}$ cluster calculated with the PBE functional.

3. Adsorption

3.1. $(TiO_2)_n$ clusters



(a)



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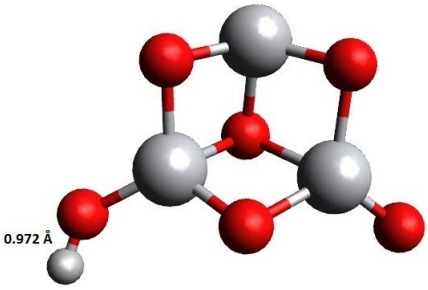

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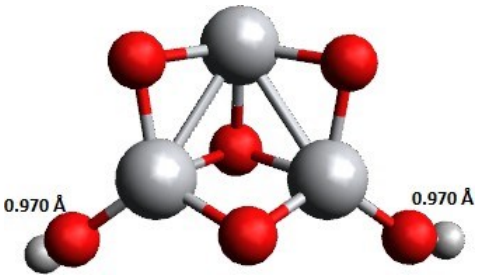

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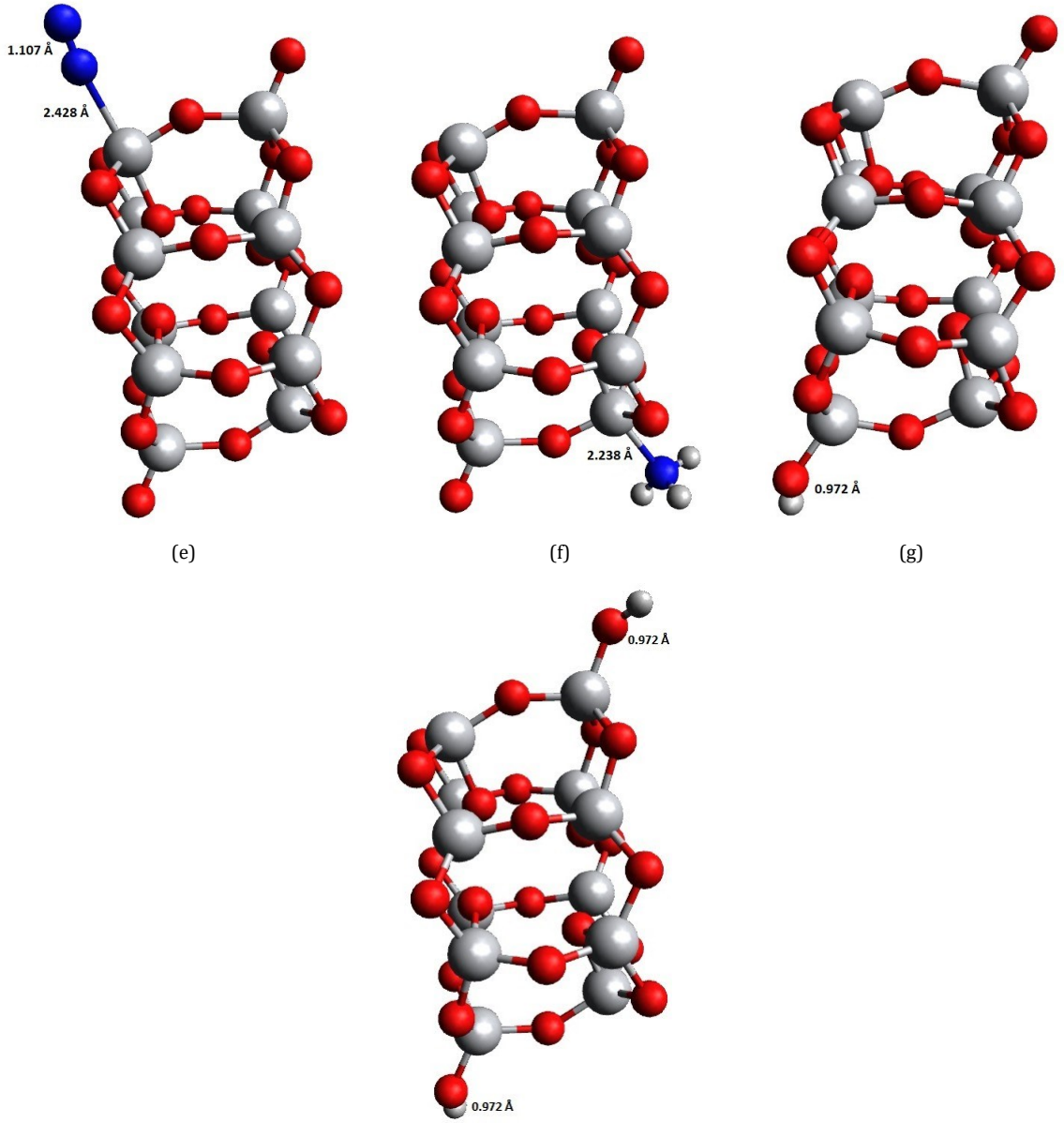


(e) (f) (g)

(h)

Figure S11: Optimized adsorption modes of a), e) N_2, b), f) NH_3, c), g) H and d), h) 2 H over $(TiO_2)_3$ and $(TiO_2)_{12}$ clusters.

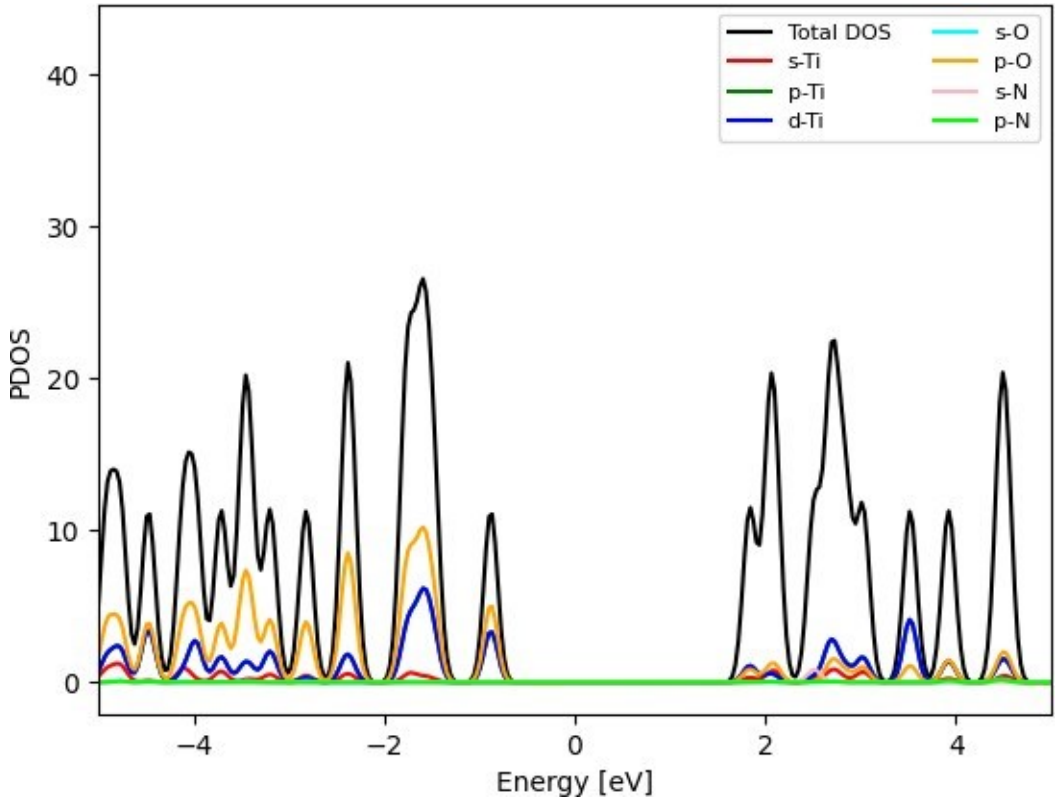


Figure S12: Total density of states and projected density of states of NH_3 adsorbed on $(TiO_2)_3$ cluster calculated with the PBE functional.

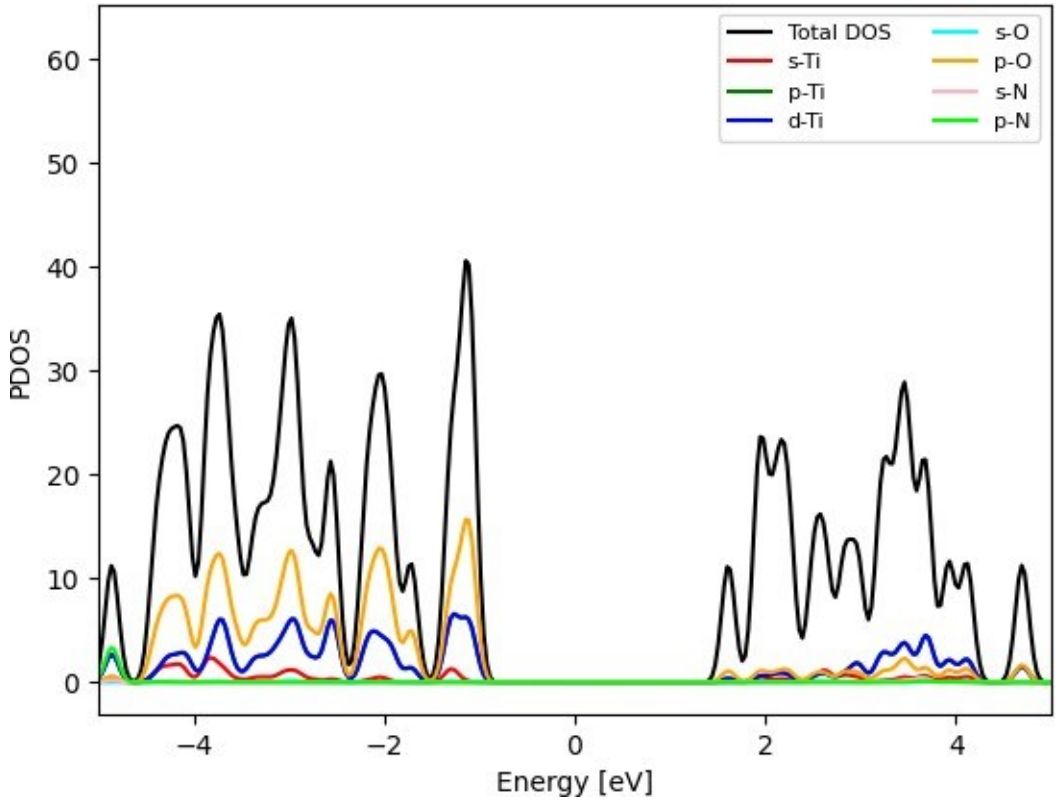


Figure S13: Total density of states and projected density of states of NH_3 adsorbed on $(TiO_2)_3$ cluster calculated with the PBE functional.

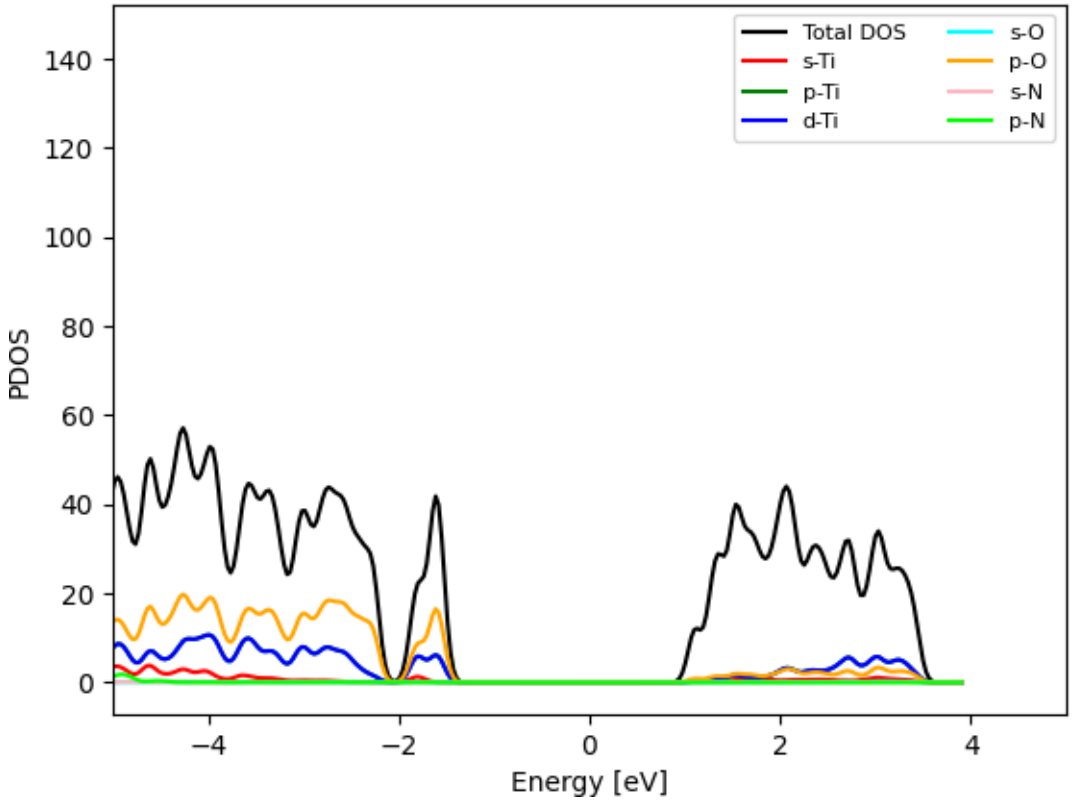
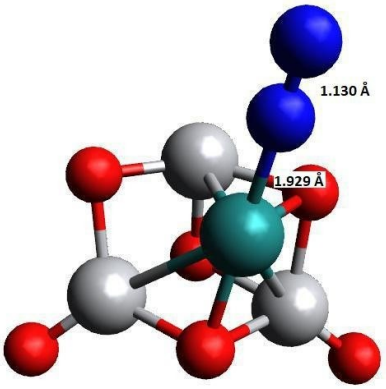
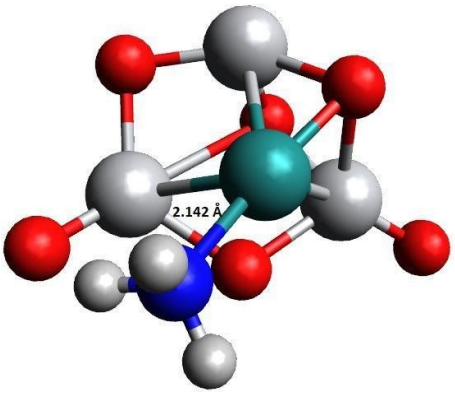


Figure S14: Total density of states and projected density of states of NH_3 adsorbed on $(TiO_2)_3$ cluster calculated with the PBE functional.

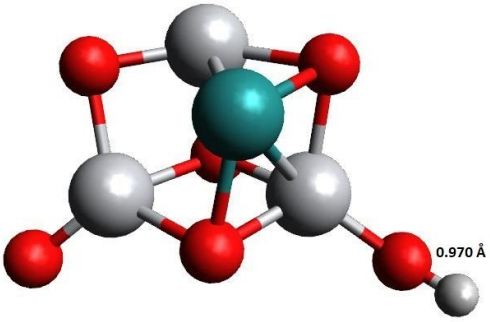
3.2. *Ru-$(TiO_2)_n$ clusters*



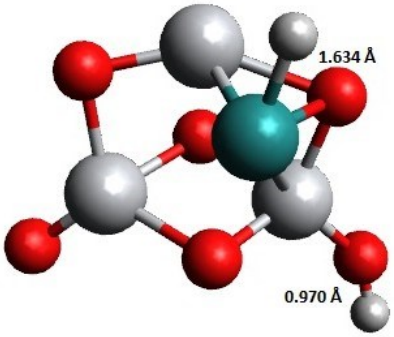
(a)



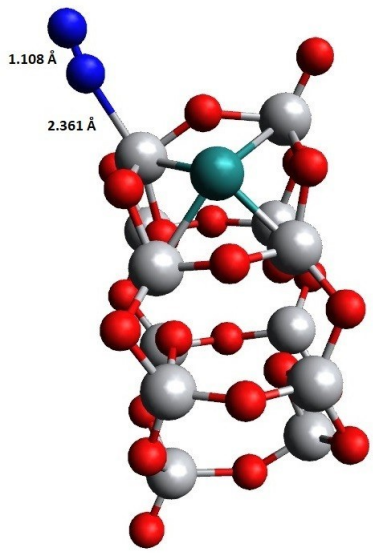
(b)



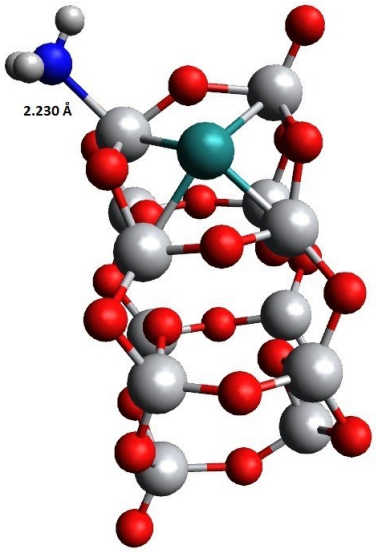
(c)



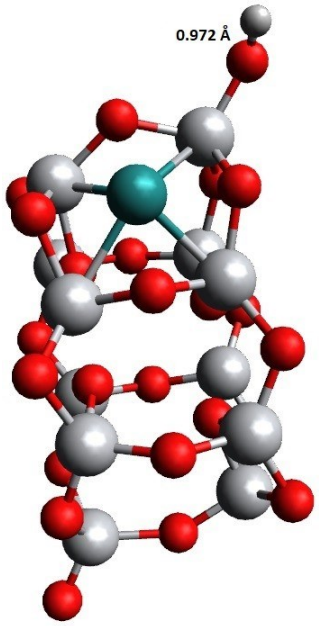
(d)



(e)



(f)



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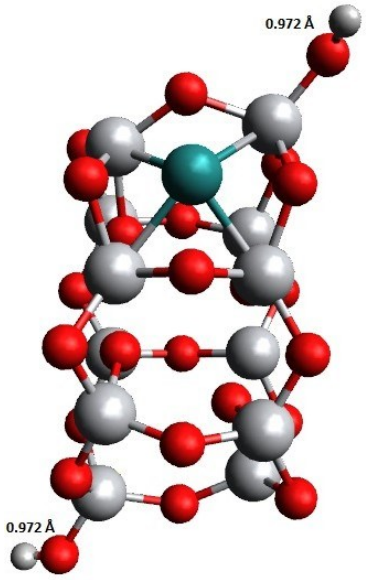

(h)

Figure S15: Optimized adsorption modes of a), e) N_2, b), f) NH_3, c), g) H and d), h) 2 H over Ru-$(TiO_2)_3$ and Ru-$(TiO_2)_{12}$ clusters.

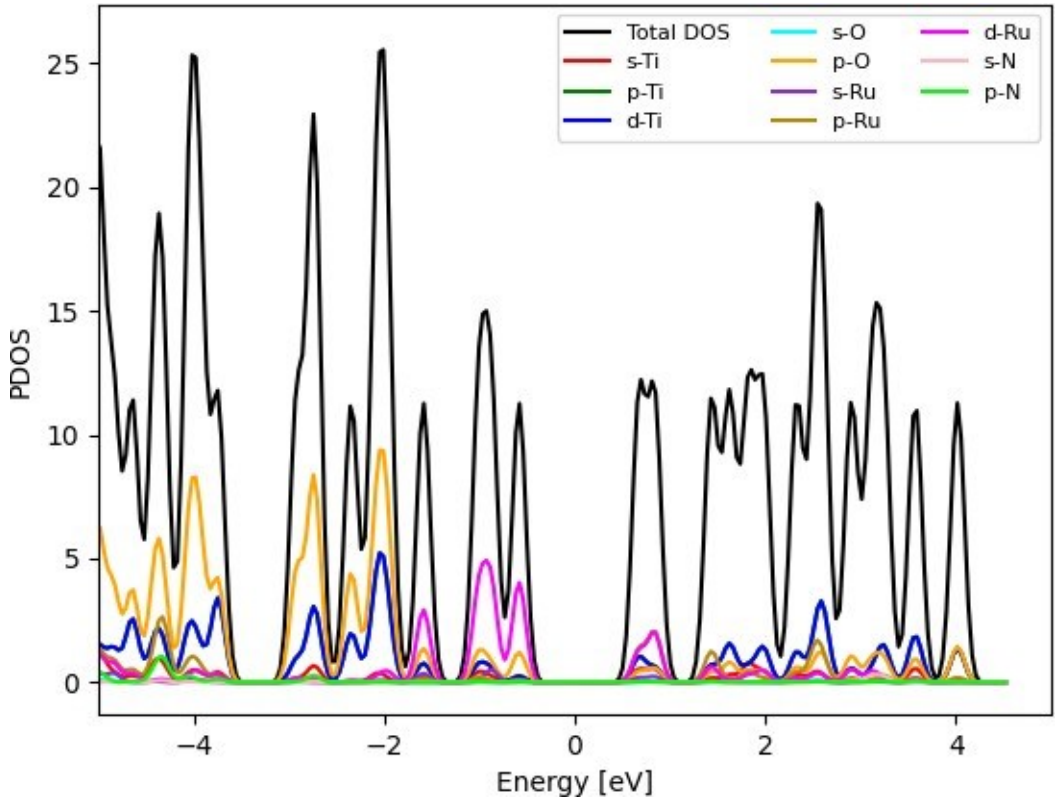

Figure S16: Total density of states and projected density of states of NH_3 adsorbed on Ru-$(TiO_2)_3$ cluster calculated with the PBE functional.

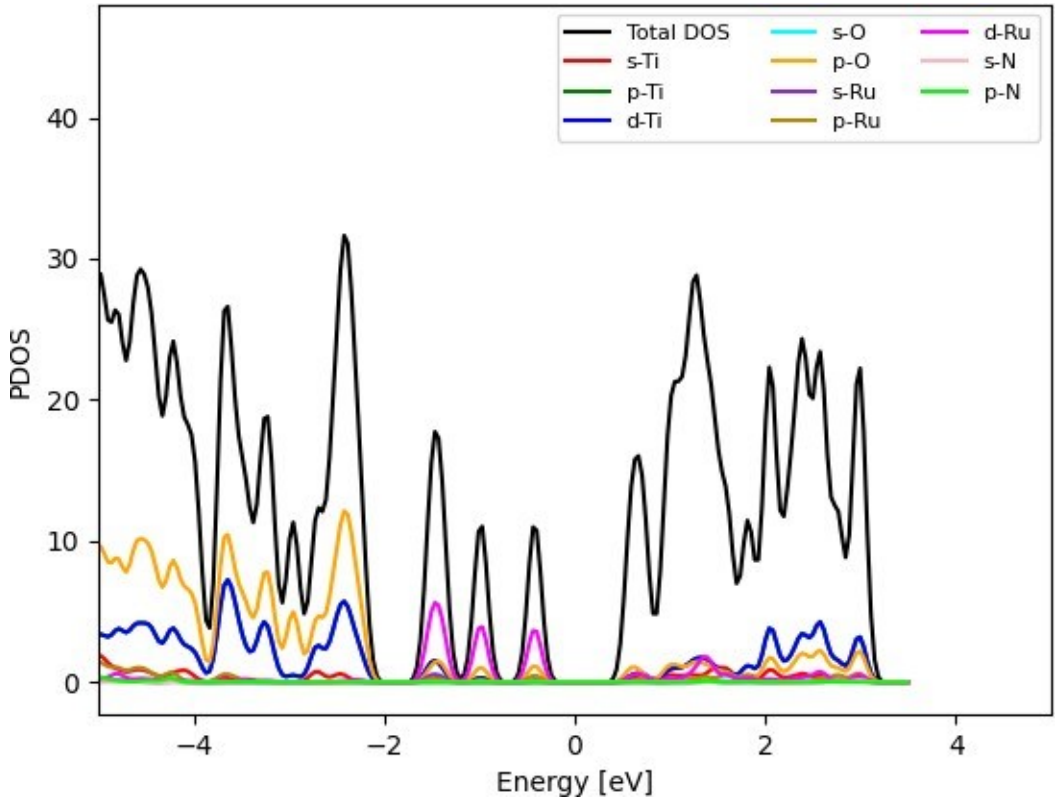

Figure S17: Total density of states and projected density of states of NH_3 adsorbed on Ru-$(TiO_2)_6$ cluster calculated with the PBE functional.

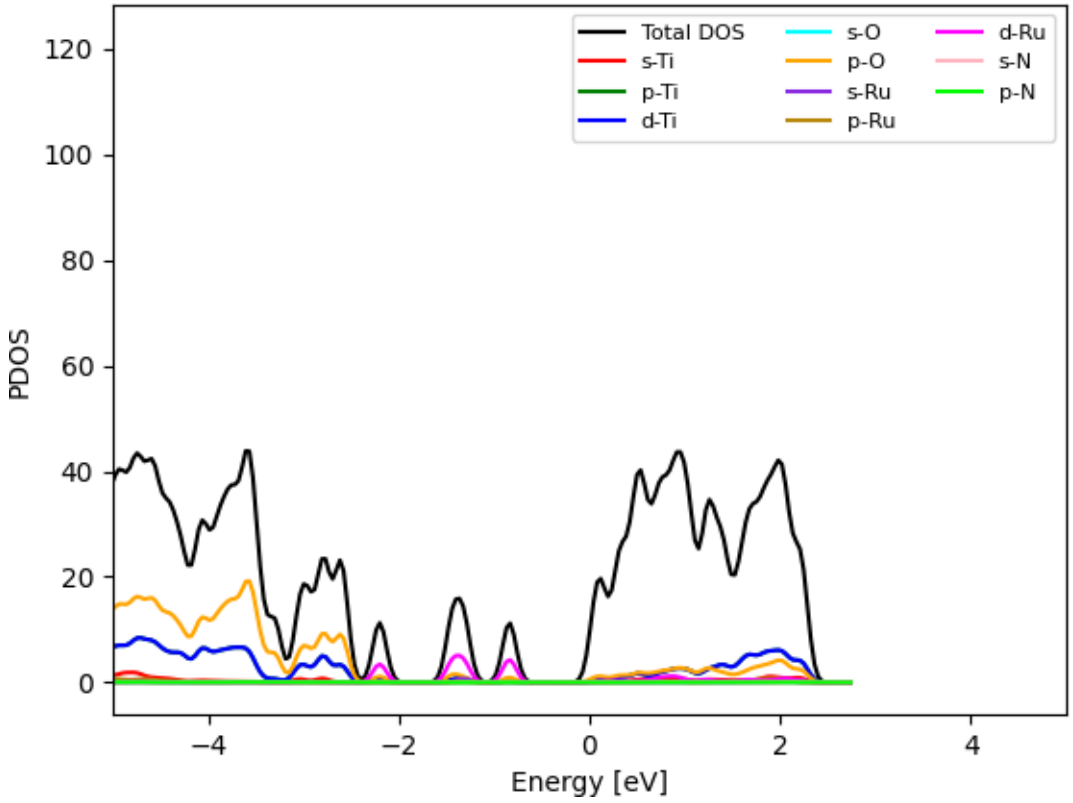

Figure S18: Total density of states and projected density of states of NH_3 adsorbed on Ru-$(TiO_2)_{12}$ cluster calculated with the PBE functional.