

This is the preprint of the following article:

Žibert T, Likozar B, Huš M. Pristine and ruthenium-doped TiO₂ nanoclusters for nitrogen reduction reaction : Ab initio study of structure and adsorption. *Fuel*. 2023;(334):1-11. doi:10.1016/j.fuel.2022.126451

which has been published in final form at:

<http://dx.doi.org/10.1016/j.fuel.2022.126451>

Supplementary Information

Pristine and ruthenium-doped TiO₂ nanoclusters for nitrogen fixation: First-principles modeling of structure and adsorption

Taja Žibert^{a,b}, Blaž Likozar^{a,*}, Matej Huš^{a,b,c,**}

^aNational Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

^bUniversity of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia

^cAssociation for Technical Culture (ZOTKS), Zaloška 65, SI-1001 Ljubljana, Slovenia

List of Figures

| | | |
|----|--|---|
| 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 | 4 |
| S2 | HOMO and LUMO orbitals of TiO ₂ clusters at an isovalence of $\pm 0.02 e_0/\text{\AA}^3$. a) HOMO of (TiO ₂) ₃ b) LUMO of (TiO ₂) ₃ c) HOMO of (TiO ₂) ₁₂ d) LUMO of (TiO ₂) ₁₂ | 5 |
| 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 | 7 |
| S4 | HOMO and LUMO orbitals of Ru-TiO ₂ clusters at an isovalence of $\pm 0.02 e_0/\text{\AA}^3$. 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 | 8 |

*Corresponding author

**Corresponding author

Email addresses: blaz.likozar@ki.si (Blaž Likozar), matej.hus@ki.si (Matej Huš)

| | | |
|-----|--|----|
| S5 | HOMO and LUMO positions relative to the Fermi level (0.0 eV) of TiO ₂ clusters calculated with PBE and HSE06 functionals. | 9 |
| S6 | Total density of states and projected density of states of the (TiO ₂) ₃ cluster calculated with PBE and HSE06 functionals. | 10 |
| S7 | Total density of states and projected density of states of the (TiO ₂) ₁₂ cluster calculated with the PBE functional. | 11 |
| S8 | HOMO and LUMO positions relative to the Fermi level (0.0 eV) of Ru-TiO ₂ clusters calculated with PBE and HSE06 functionals. | 12 |
| S9 | Total density of states and projected density of states of the Ru-(TiO ₂) ₃ cluster calculated with PBE and HSE06 functionals. | 13 |
| S10 | Total density of states and projected density of states of the Ru-(TiO ₂) ₁₂ cluster calculated with the PBE functional. | 14 |
| 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. | 16 |
| S12 | Total density of states and projected density of states of NH ₃ adsorbed on (TiO ₂) ₃ cluster calculated with the PBE functional. | 17 |
| S13 | Total density of states and projected density of states of NH ₃ adsorbed on (TiO ₂) ₃ cluster calculated with the PBE functional. | 18 |
| S14 | Total density of states and projected density of states of NH ₃ adsorbed on (TiO ₂) ₃ cluster calculated with the PBE functional. | 19 |
| 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. | 21 |
| 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. | 22 |

| | | |
|-----|---|----|
| 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. | 23 |
| 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..... | 24 |

1. Optimized structures

1.1. $(\text{TiO}_2)_n$ clusters

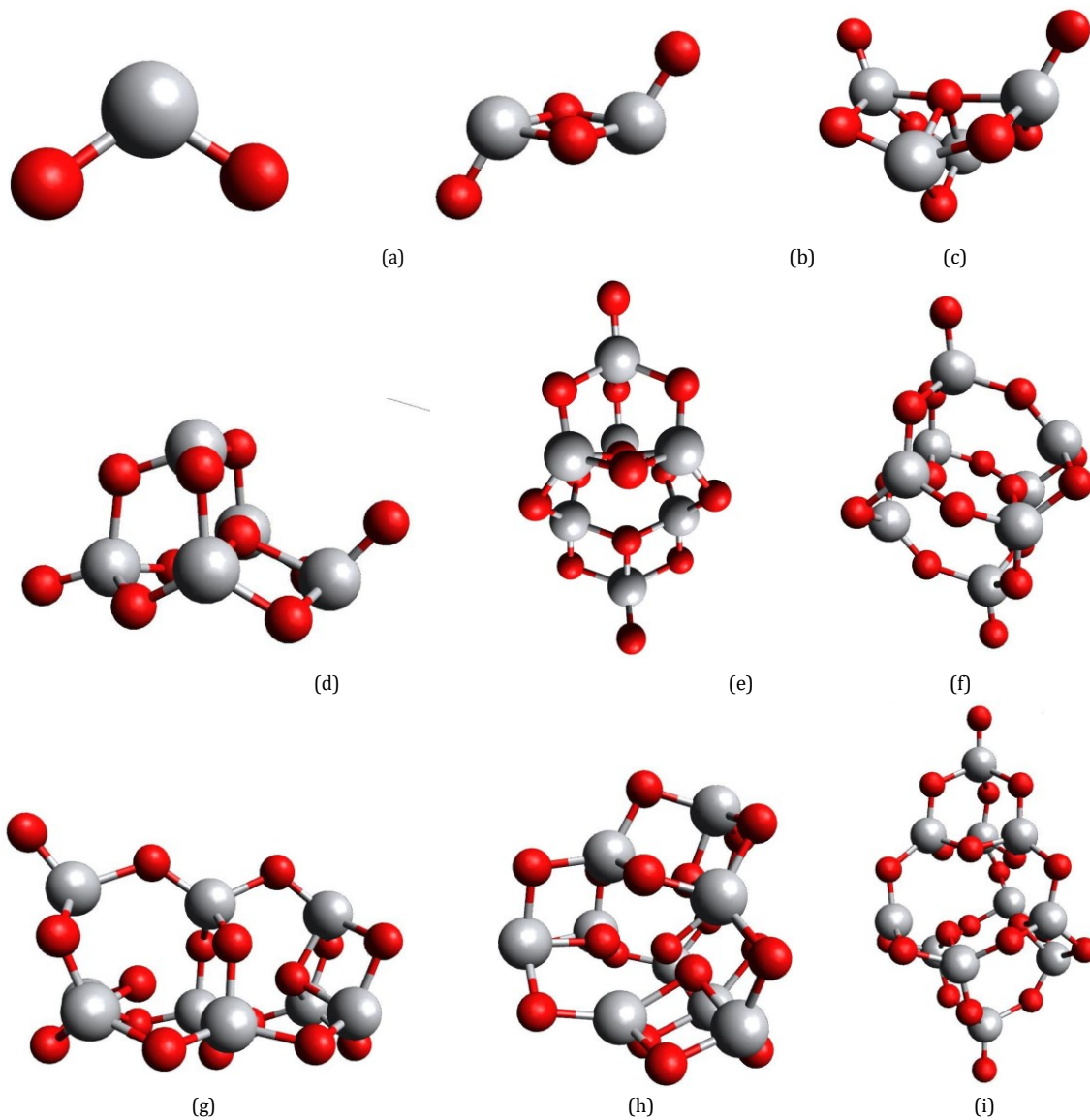


Figure S1: Optimized structures of a) $(\text{TiO}_2)_1$, b) $(\text{TiO}_2)_2$, c) $(\text{TiO}_2)_4$, d) $(\text{TiO}_2)_5$, e) $(\text{TiO}_2)_7$, f) $(\text{TiO}_2)_8$, g) $(\text{TiO}_2)_9$, h) $(\text{TiO}_2)_{10}$, i) $(\text{TiO}_2)_{11}$

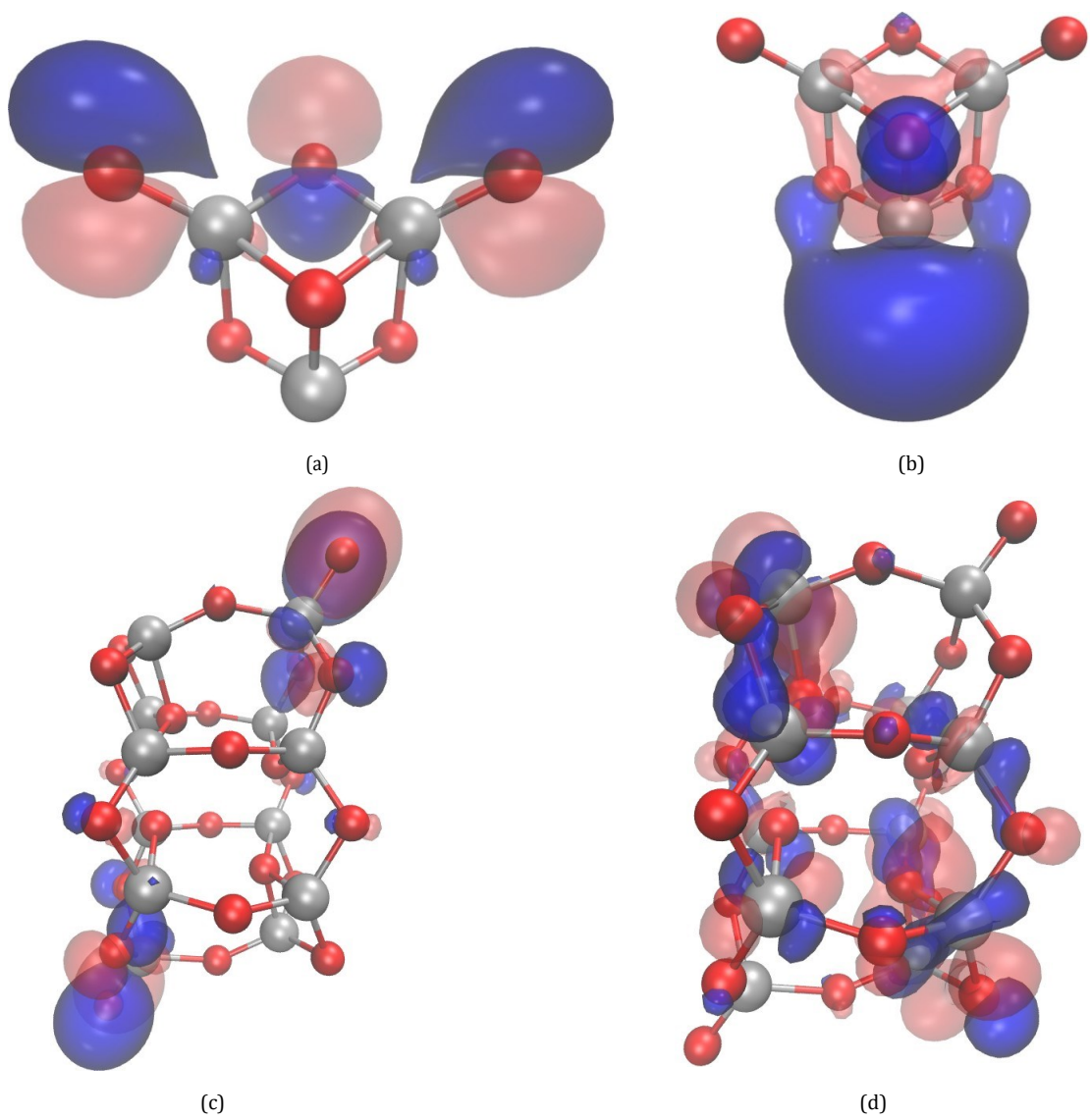
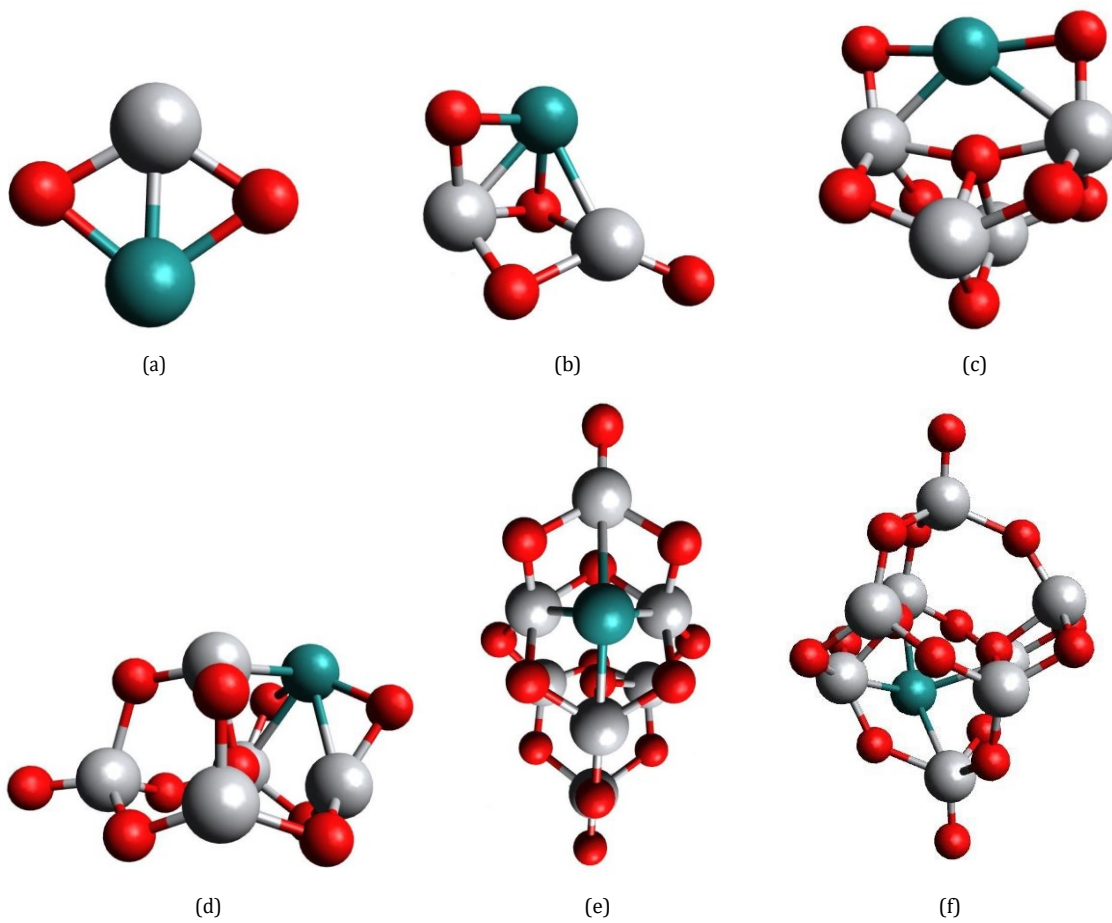


Figure S2: HOMO and LUMO orbitals of TiO_2 clusters at an isovalue of $\pm 0.02 e_0/\text{\AA}^3$. a) HOMO of $(\text{TiO}_2)_3$ b) LUMO of $(\text{TiO}_2)_3$ c) HOMO of $(\text{TiO}_2)_{12}$ d) LUMO of $(\text{TiO}_2)_{12}$.

1.2. $Ru-(TiO_2)_n$ clusters



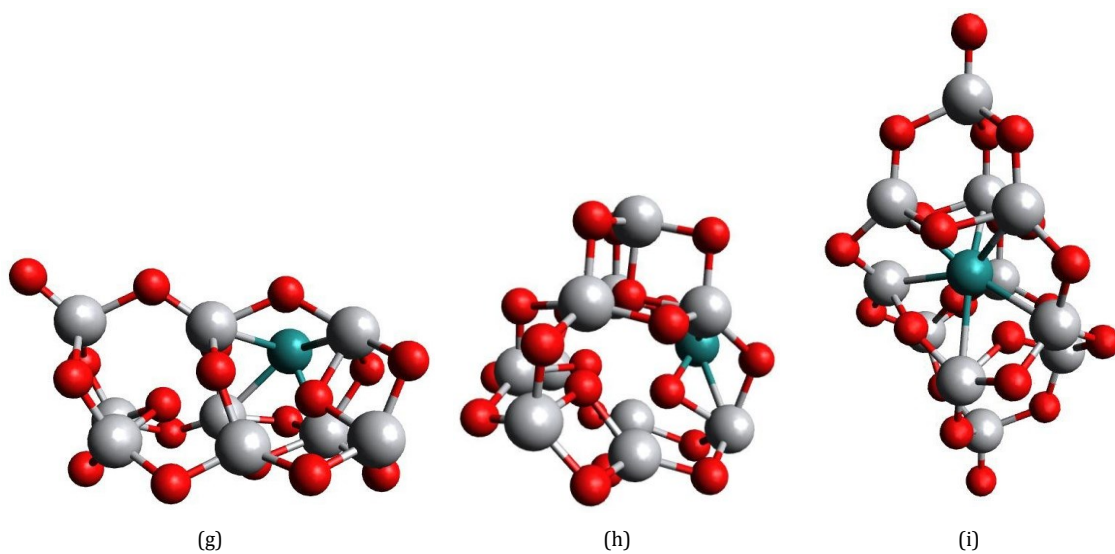


Figure S3: Optimized structures of a) Ru-(TiO₂)₁, b) Ru-(TiO₂)₂, c) Ru-(TiO₂)₄, d) Ru-(TiO₂)₅, e) Ru-(TiO₂)₇, f) Ru-(TiO₂)₈, g) Ru-(TiO₂)₉, h) Ru-(TiO₂)₁₀, i) Ru-(TiO₂)₁₁.

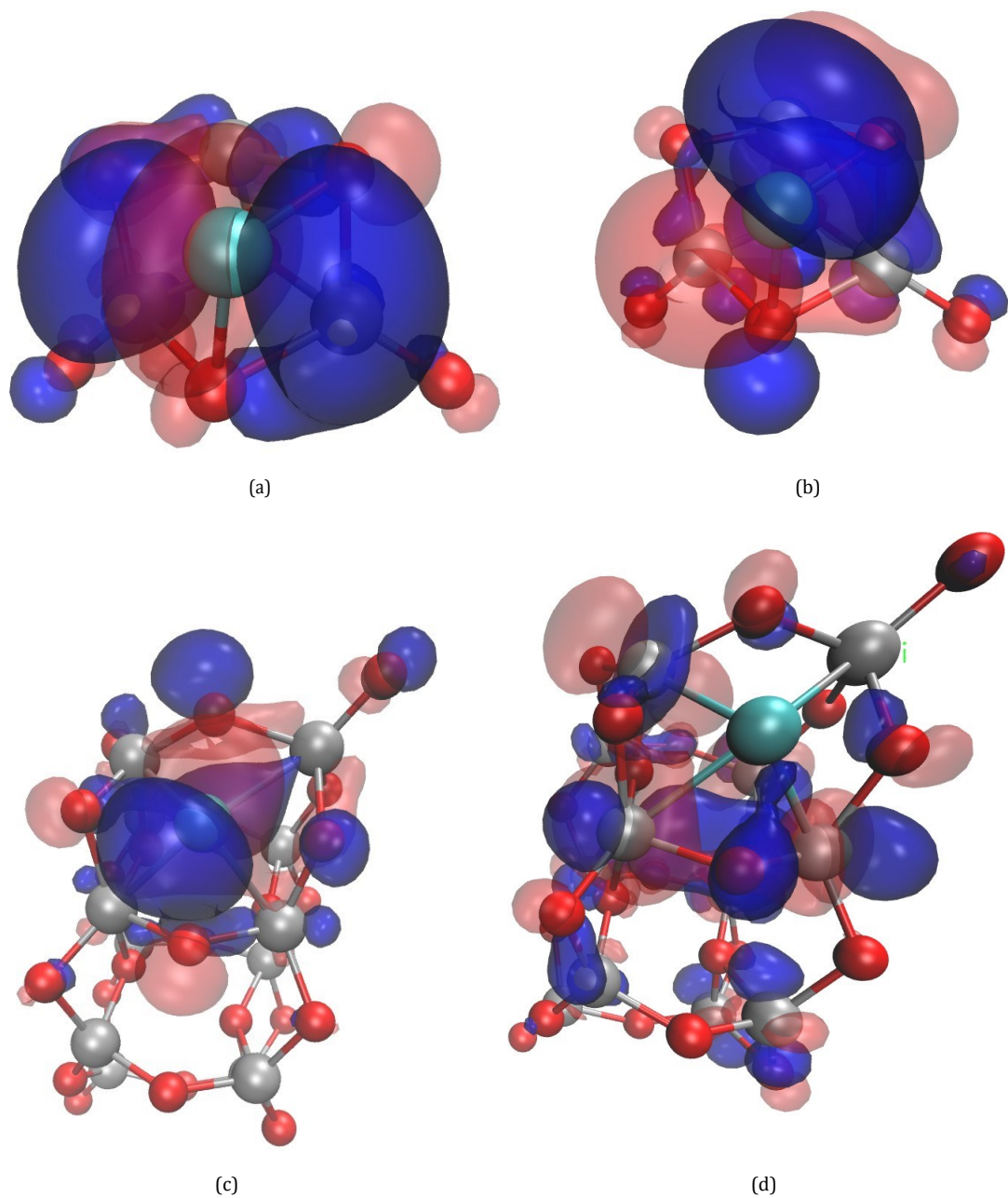


Figure S4: HOMO and LUMO orbitals of Ru-TiO₂ clusters at an isovalue of $\pm 0.02 e_0/\text{\AA}^3$. a) HOMO of Ru-(TiO₂)₃ b) LUMO of Ru-(TiO₂)₃ c) HOMO of Ru-(TiO₂)₁₂ d) LUMO of Ru-(TiO₂)₁₂.

2. Electronic properties

2.1. $(\text{TiO}_2)_n$ clusters

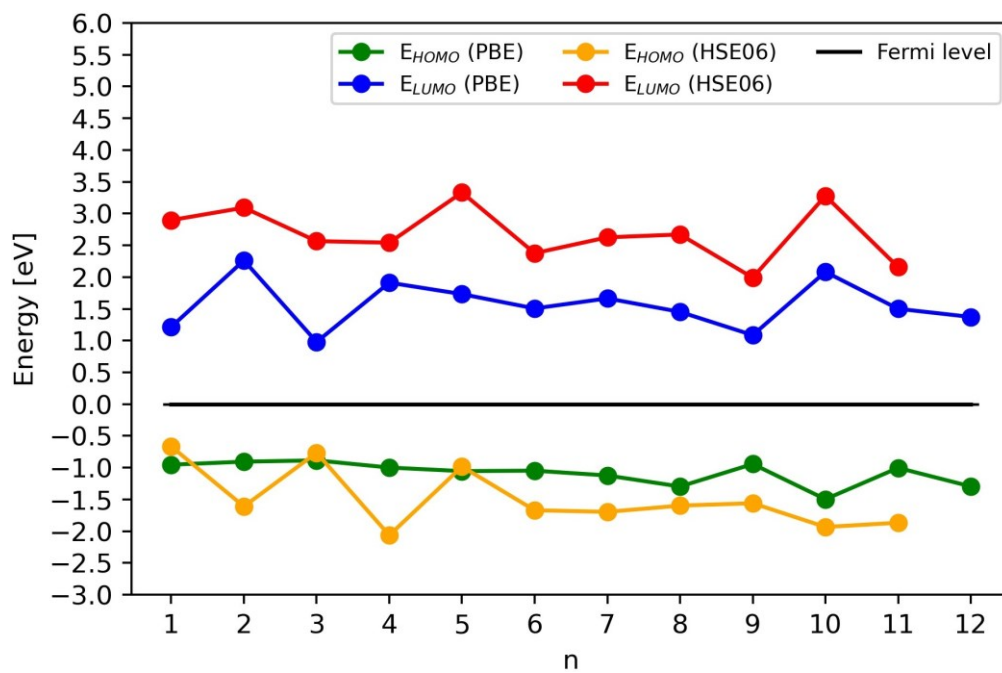
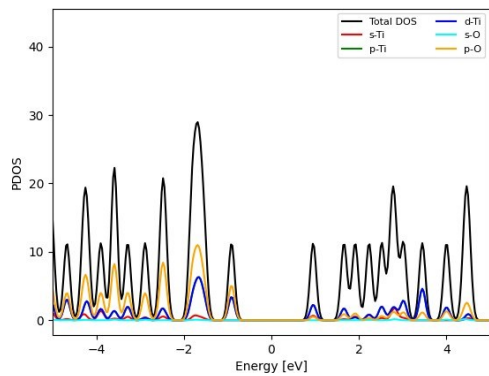
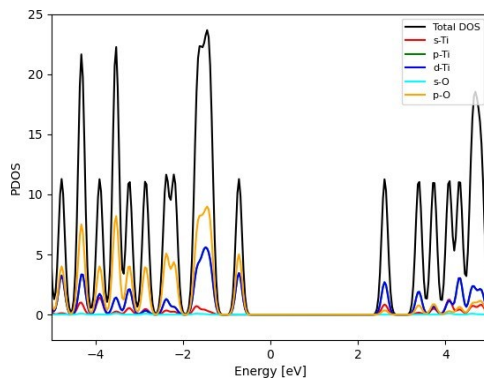


Figure S5: HOMO and LUMO positions relative to the Fermi level (0.0 eV) of TiO_2 clusters calculated with PBE and HSE06 functionals.



(a) PBE functional



(b) HSE functional

Figure S6: Total density of states and projected density of states of the $(\text{TiO}_2)_3$ cluster calculated with PBE and HSE06 functionals.

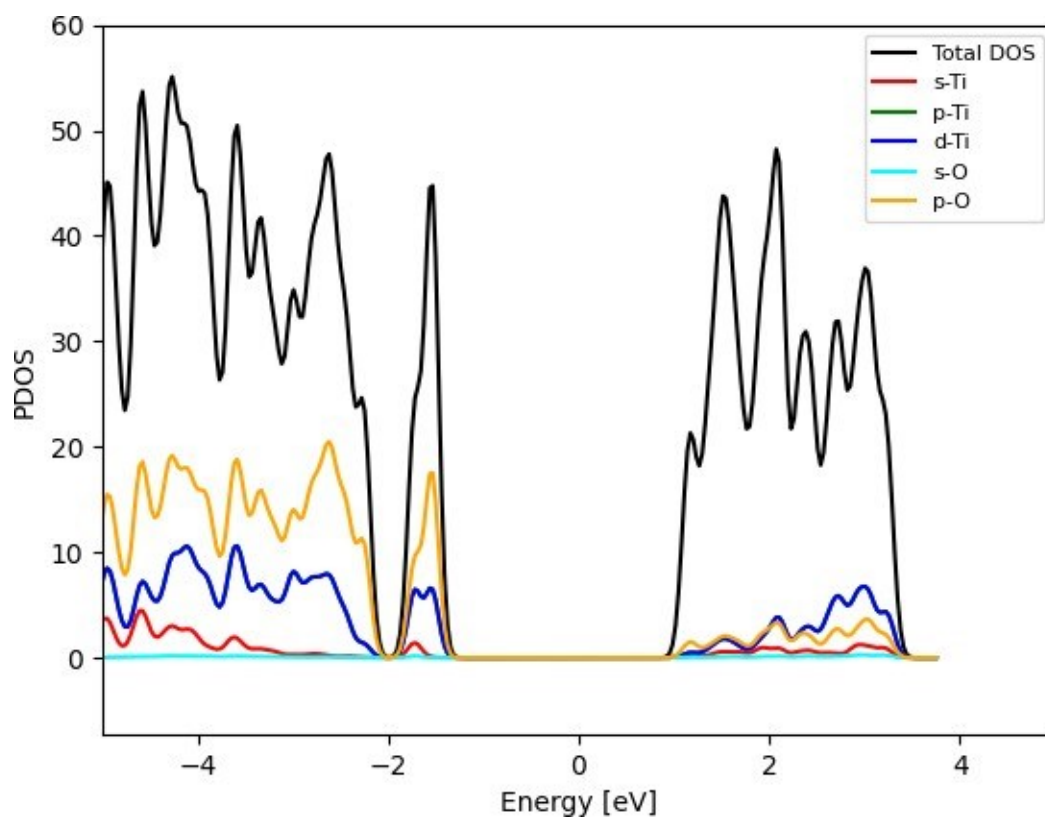


Figure S7: Total density of states and projected density of states of the $(\text{TiO}_2)_{12}$ cluster calculated with the PBE functional.

2.2. Ru-(TiO₂)_n clusters

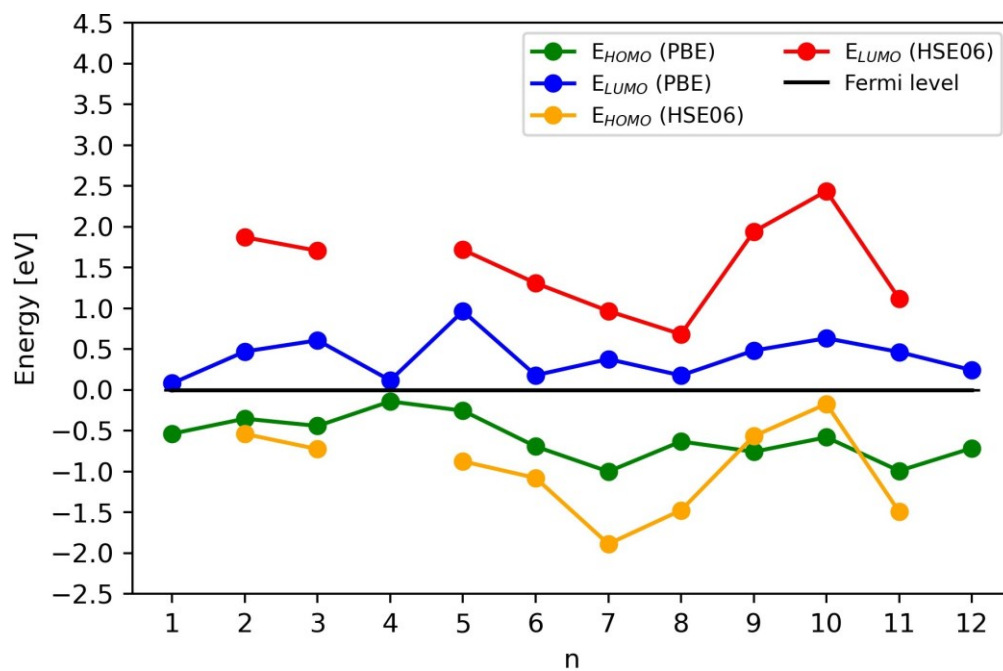
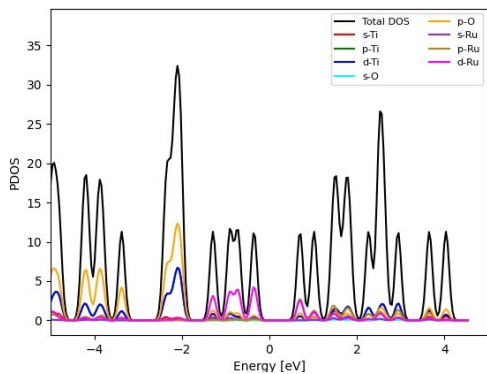
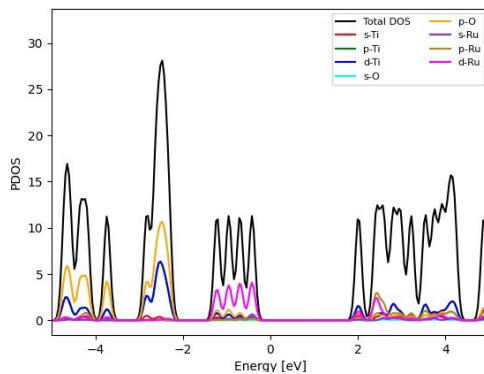


Figure S8: HOMO and LUMO positions relative to the Fermi level (0.0 eV) of Ru-TiO₂ clusters calculated with PBE and HSE06 functionals.



(a) PBE functional



(b) HSE functional

Figure S9: Total density of states and projected density of states of the Ru-(TiO₂)₃ cluster calculated with PBE and HSE06 functionals.

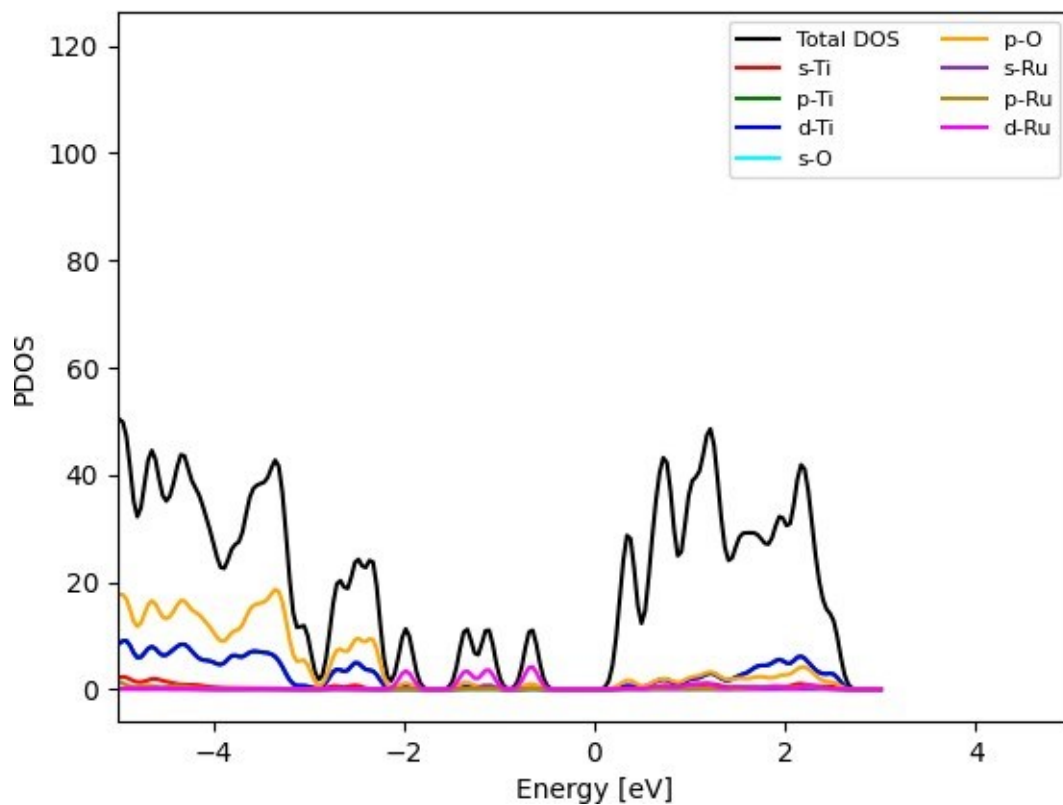
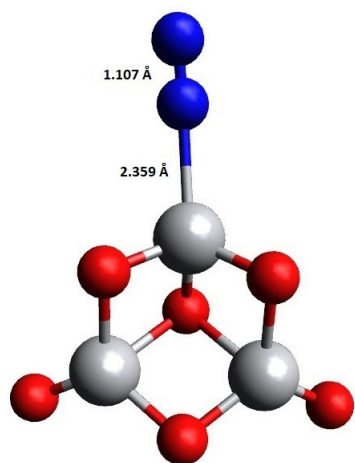


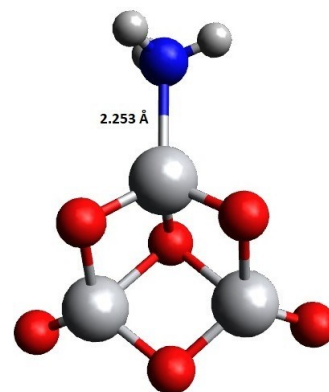
Figure S10: Total density of states and projected density of states of the Ru-(TiO₂)₁₂ cluster calculated with the PBE functional.

3. Adsorption

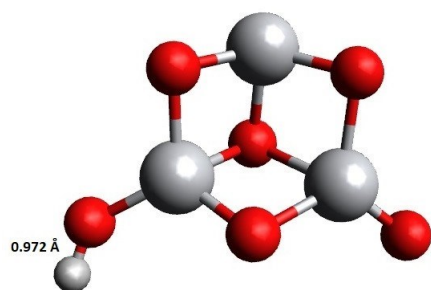
3.1. $(\text{TiO}_2)_n$ clusters



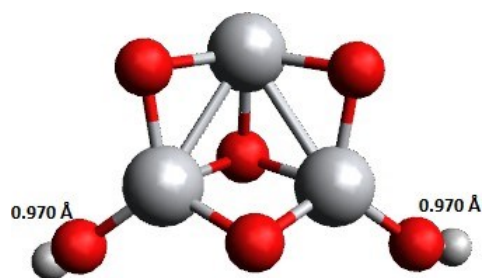
(a)



(b)



(c)



(d)

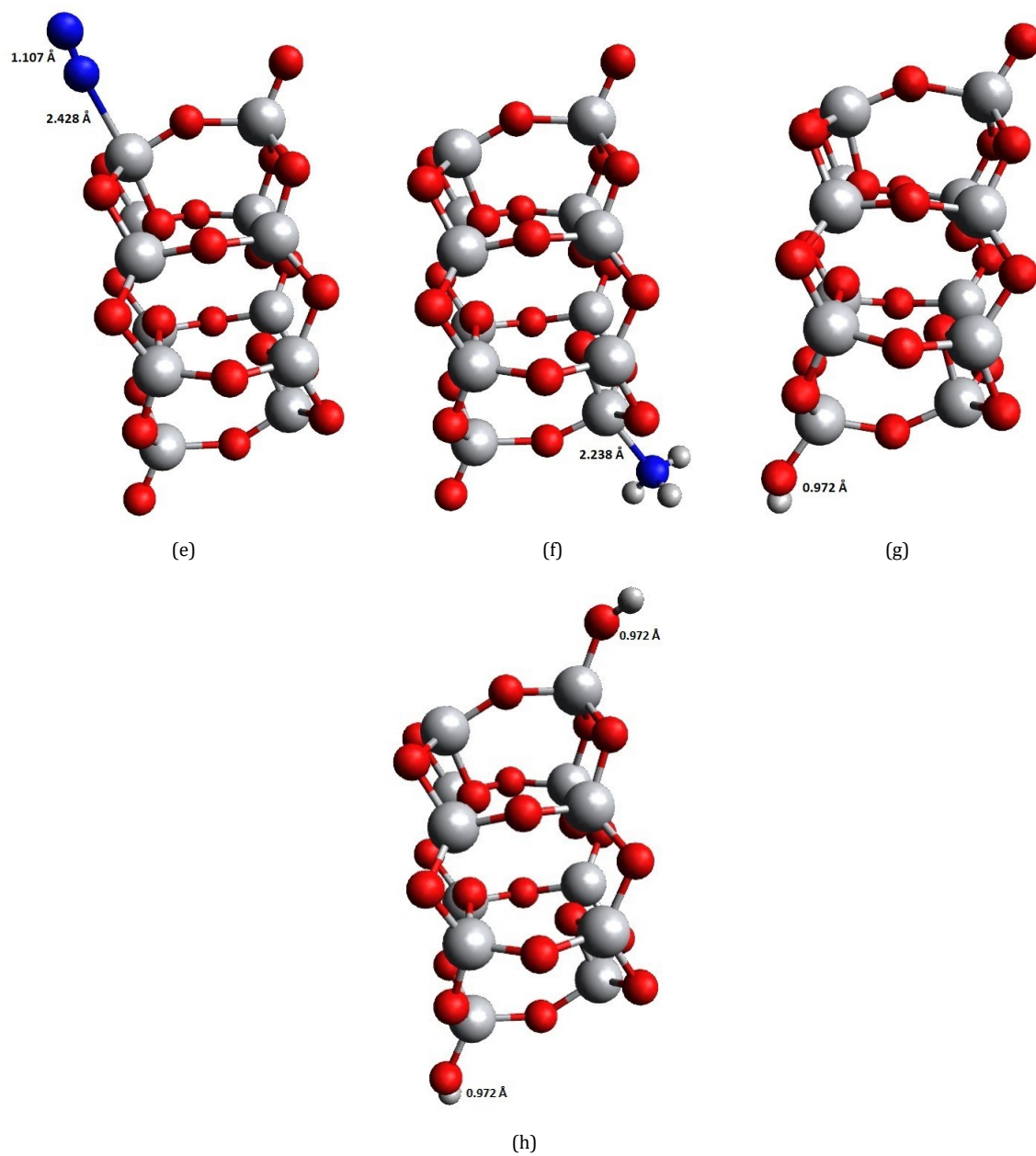


Figure S11: Optimized adsorption modes of a), e) N_2 , b), f) NH_3 , c), g) H and d), h) 2 H over $(TiO_2)_3$ and $(TiO_2)_{12}$ clusters.

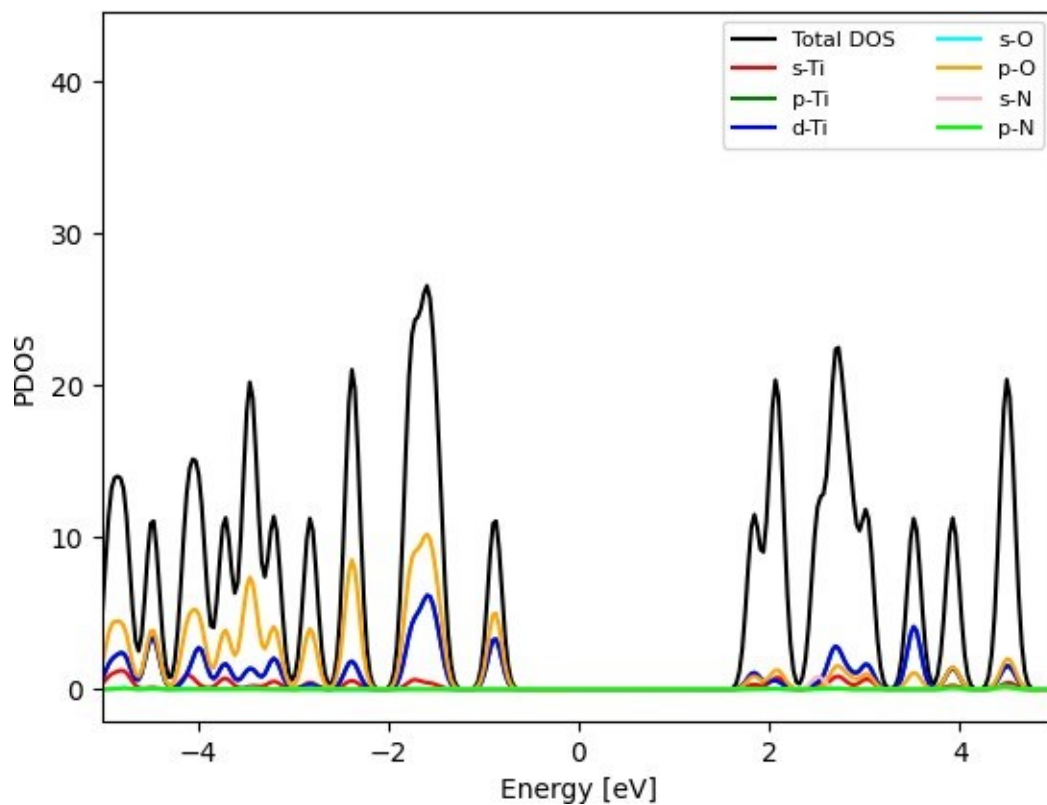


Figure S12: Total density of states and projected density of states of NH₃ adsorbed on (TiO₂)₃ cluster calculated with the PBE functional.

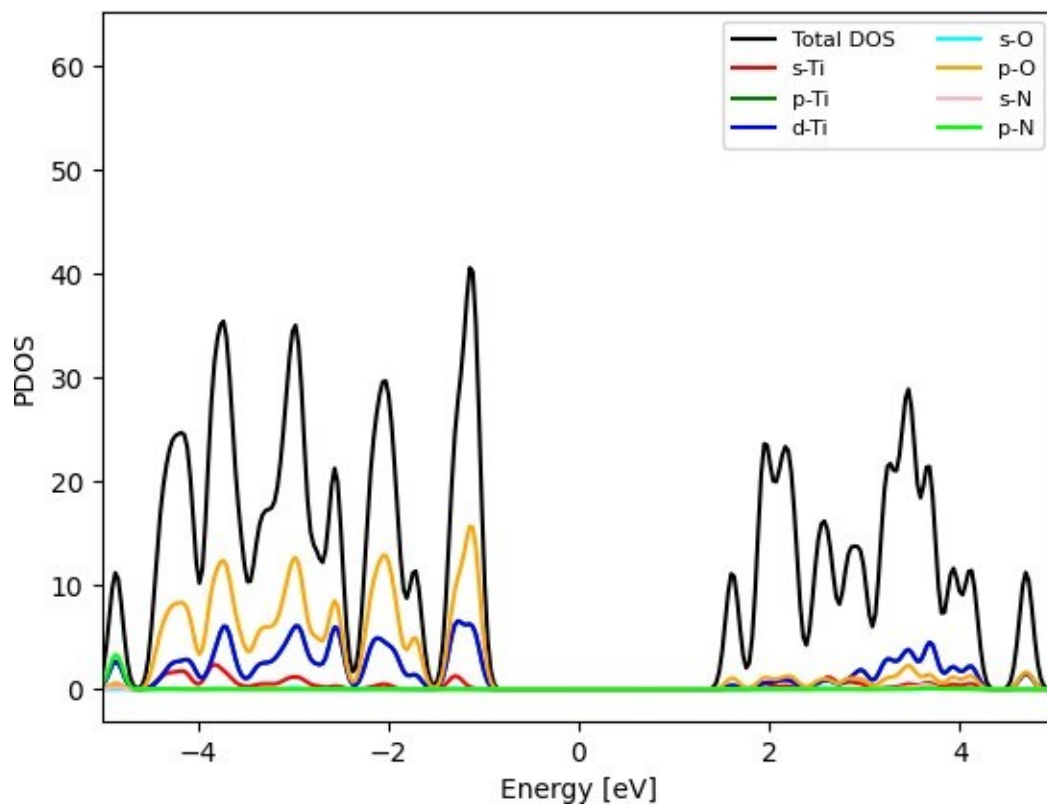


Figure S13: Total density of states and projected density of states of NH₃ adsorbed on (TiO₂)₃ cluster calculated with the PBE functional.

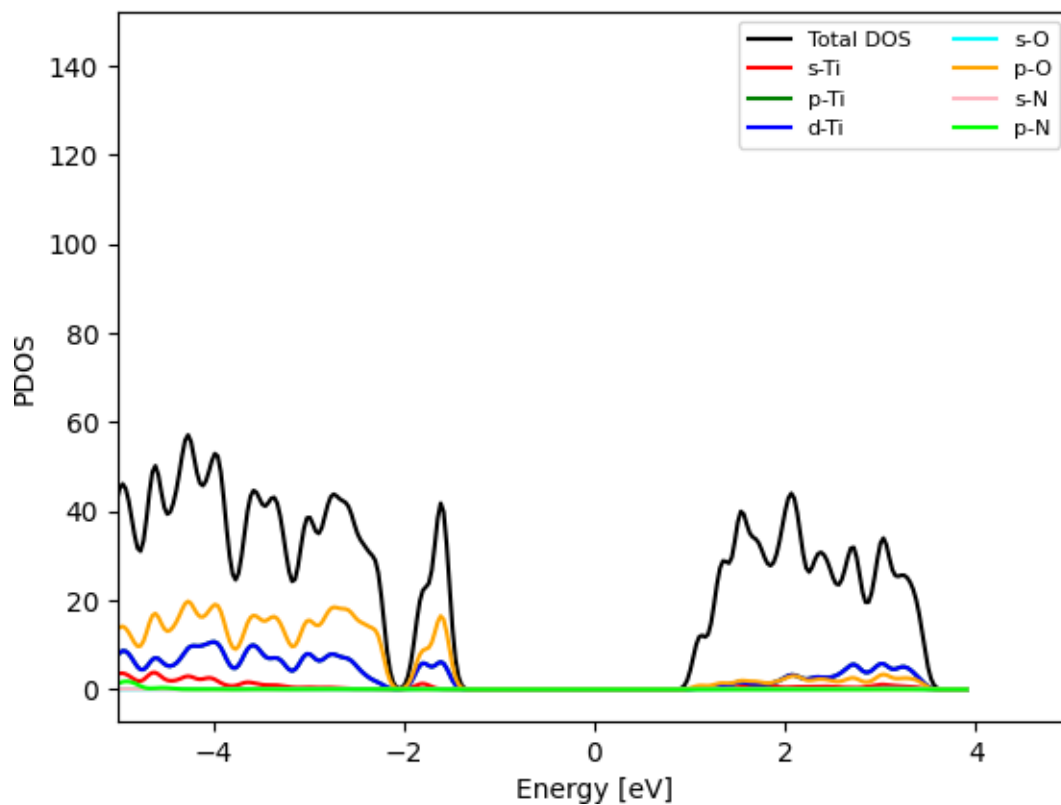
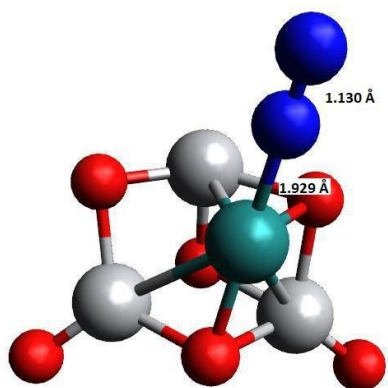
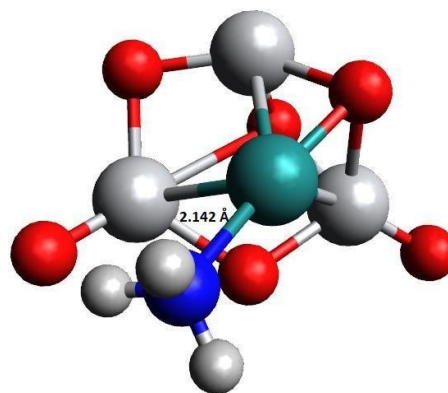


Figure S14: Total density of states and projected density of states of NH₃ adsorbed on (TiO₂)₃ cluster calculated with the PBE functional.

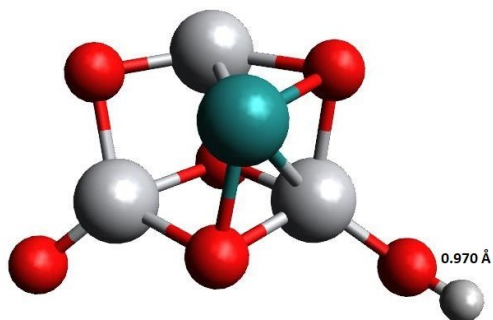
3.2. $Ru-(TiO_2)_n$ clusters



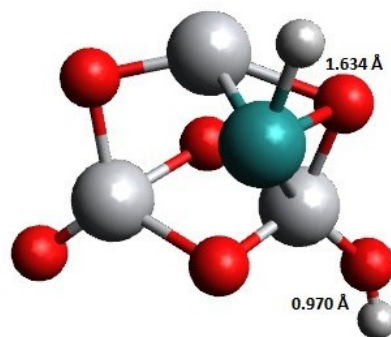
(a)



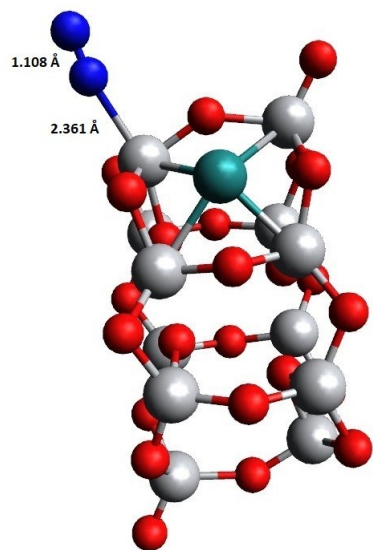
(b)



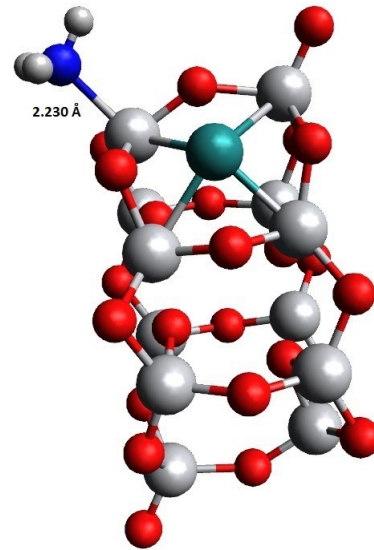
(c)



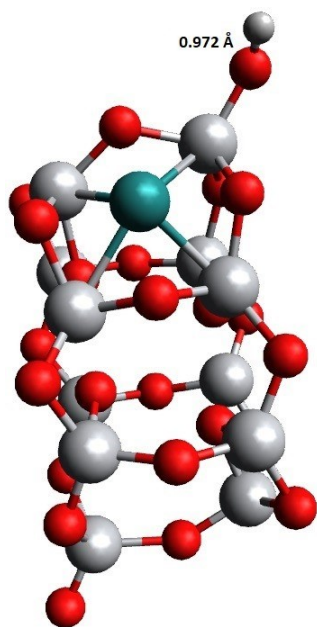
(d)



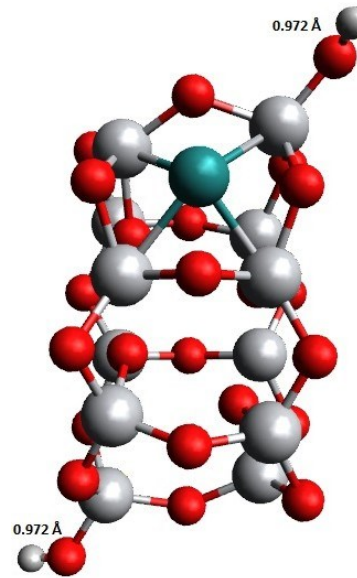
(e)



(f)



(g)



(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.

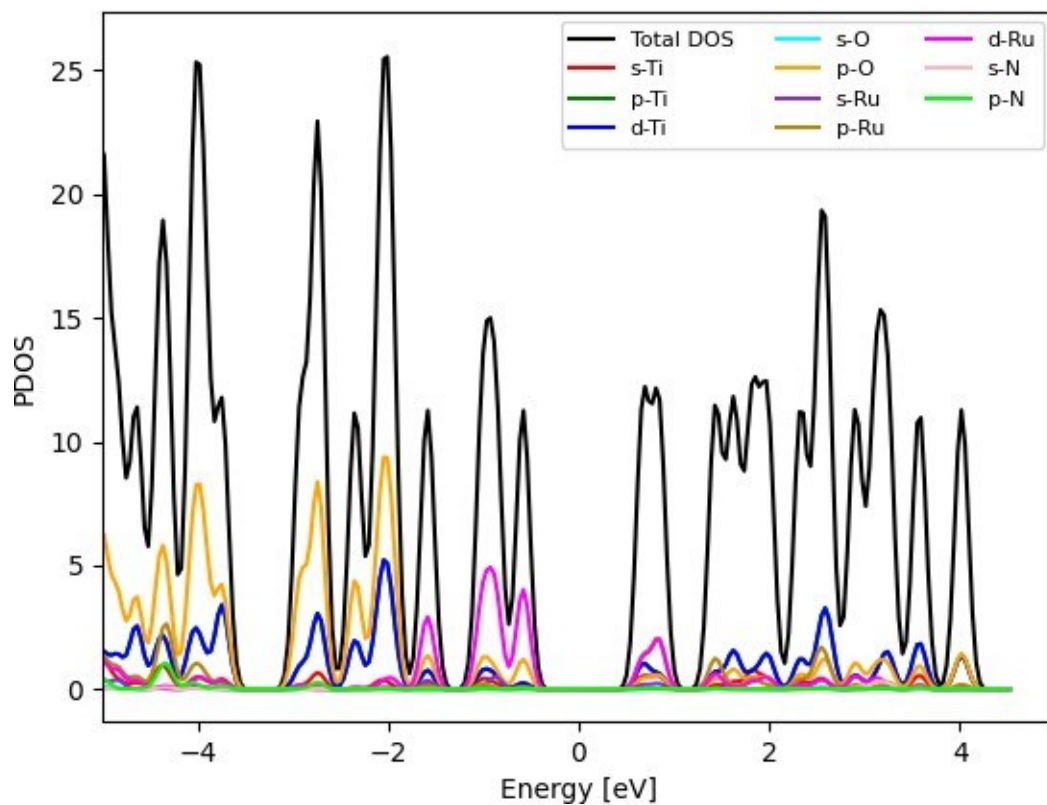


Figure S16: Total density of states and projected density of states of NH₃ adsorbed on Ru-(TiO₂)₃ cluster calculated with the PBE functional.

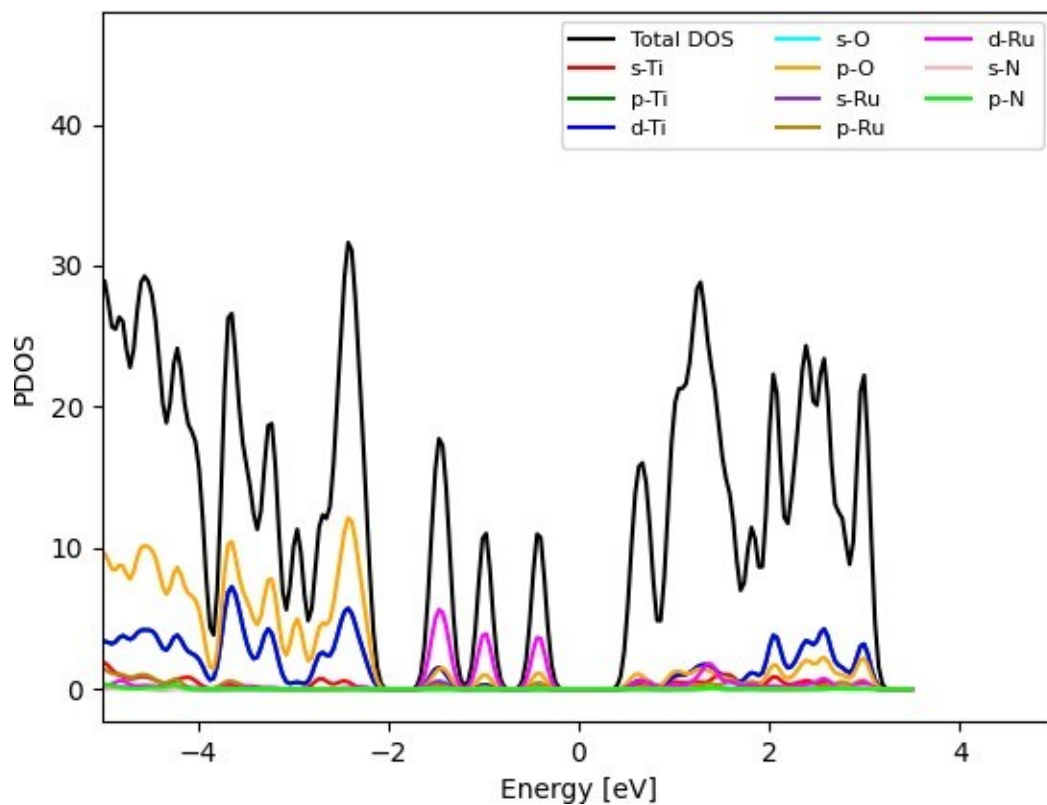


Figure S17: Total density of states and projected density of states of NH₃ adsorbed on Ru-(TiO₂)₆ cluster calculated with the PBE functional.

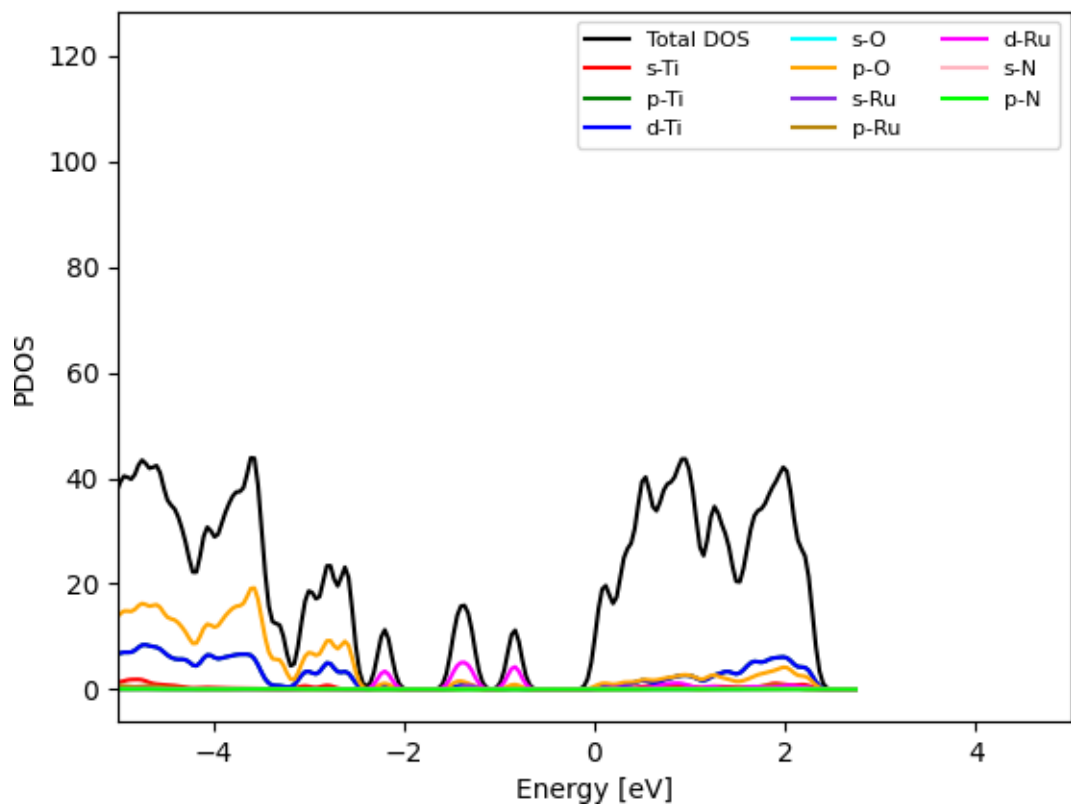


Figure S18: Total density of states and projected density of states of NH₃ adsorbed on Ru-(TiO₂)₁₂ cluster calculated with the PBE functional.