

Supporting information for:

Effect of Oxygen Vacancies on Adsorption of Small Molecules on Anatase and Rutile TiO₂ Surfaces:
A Frontier Orbital Approach

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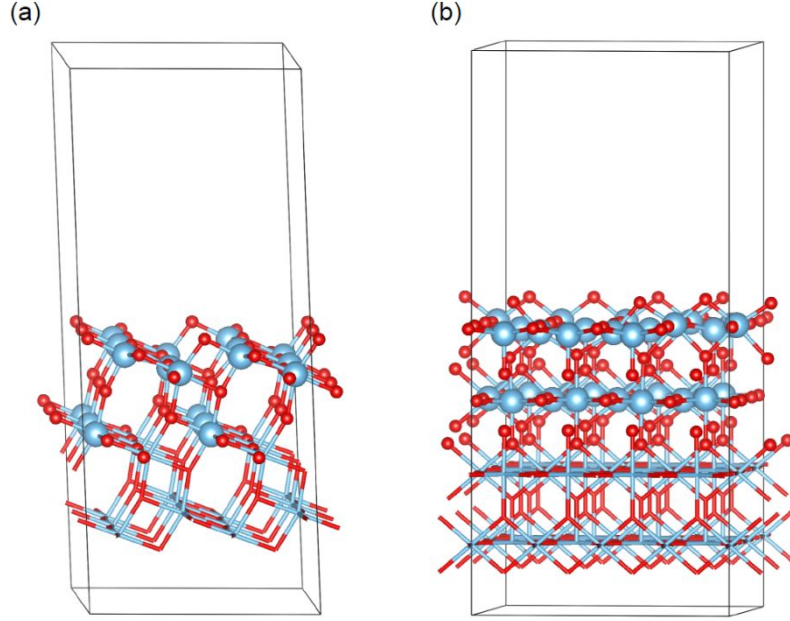


Figure S1. The structures of (a) anatase and (b) rutile TiO_2 surface models. The Ti and O atoms are colored blue and red, respectively. The atoms represented by a stick are fixed ones for the optimization.

Details of surface energy computations

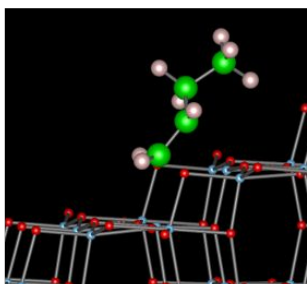
The surface energy (E_{surf}) is defined as

$$E_{\text{surf}} = (E_{\text{slab}} - E_{\text{bulk}}) / 2A$$

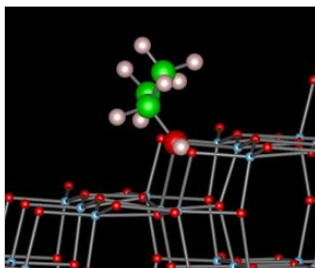
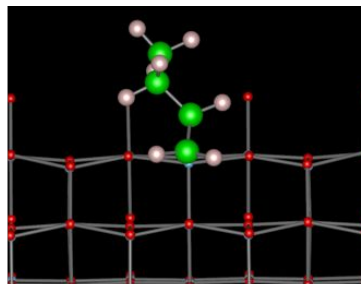
where E_{slab} and E_{bulk} are the energy of the slab and the energy of the slab constituents when in the form of a perfect bulk, respectively, and A is the in-plane area of the slab (the coefficient of 2 accounts for sides of the slab). At the PBEsol+ U level, E_{surf} values are 47 and 68 meV/Å² for anatase and rutile, respectively. The E_{Ovac} is defined as

$$E_{\text{Ovac}} = E_{\text{removed}} - E_{\text{slab}} + \mu_{\text{O}}$$

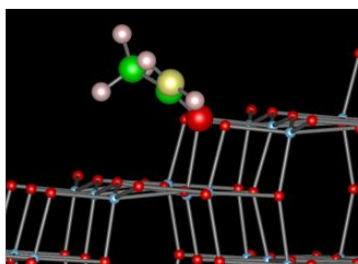
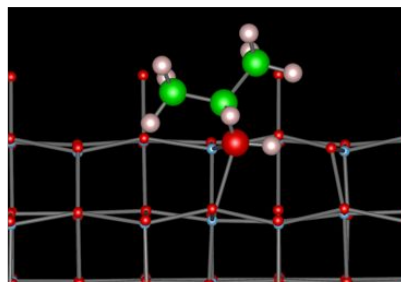
where E_{removed} and μ_{O} are the energy of the slab when an O atom are removed and the chemical potential of the O that is removed. The chemical potential is referenced to O_2 gas in the current case. The E_{Ovac} values are 4.26 and 3.52 eV for anatase and rutile, respectively. The E_{surf} and E_{Ovac} values are in agreement with the values of our previous report (ref. 60).



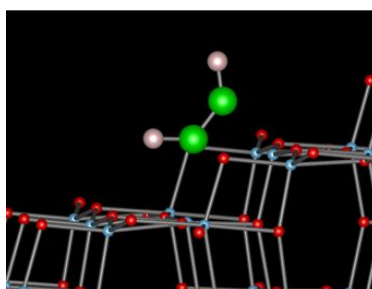
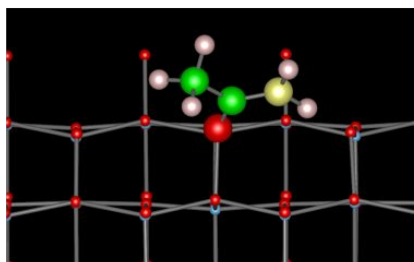
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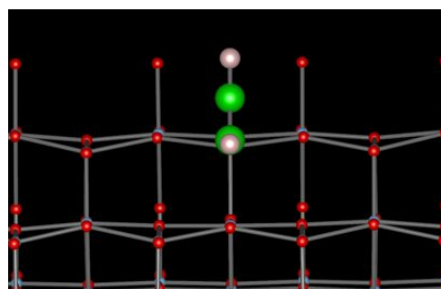
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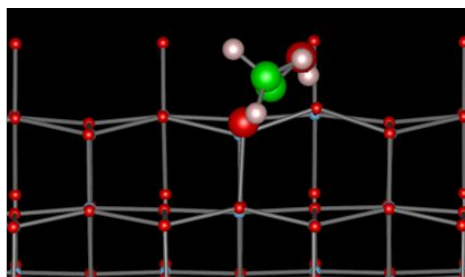
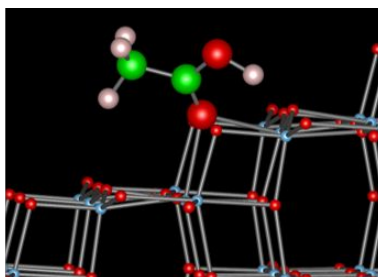


Acetamide

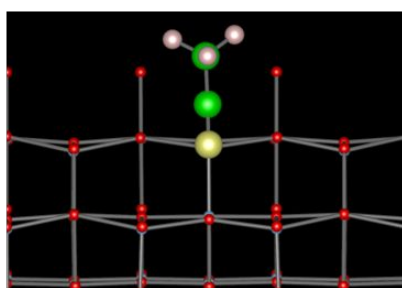
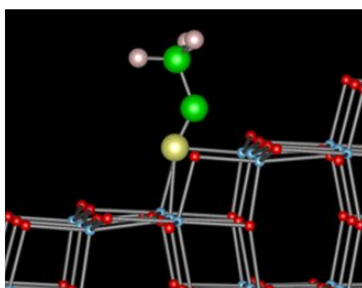


Acetylene

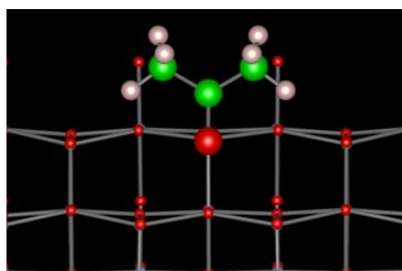
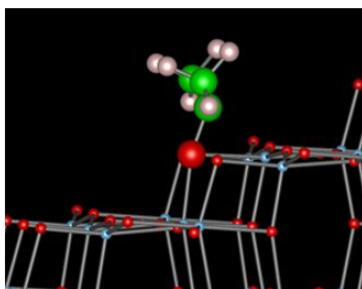




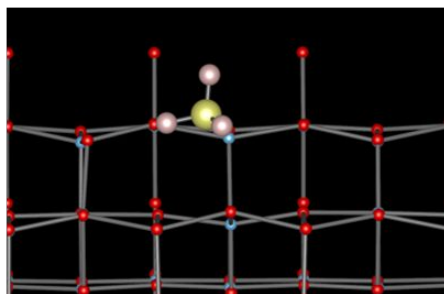
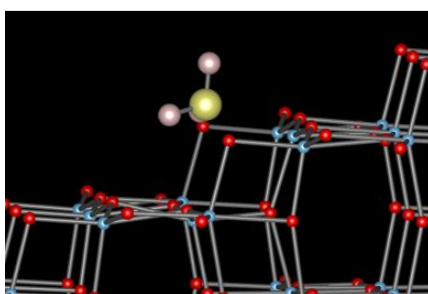
Acetic acid



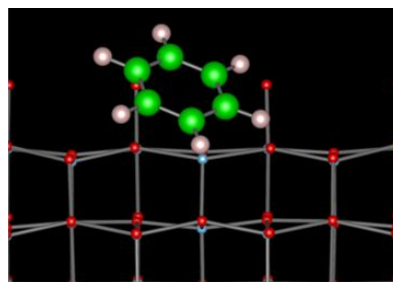
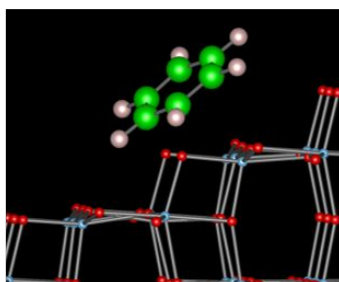
Acetonitrile



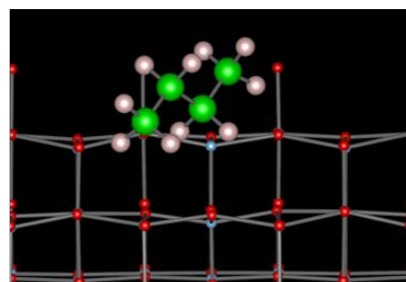
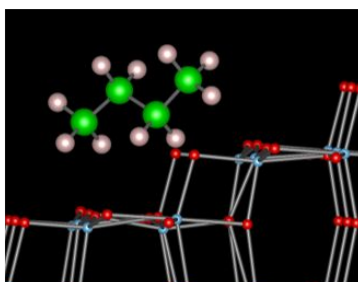
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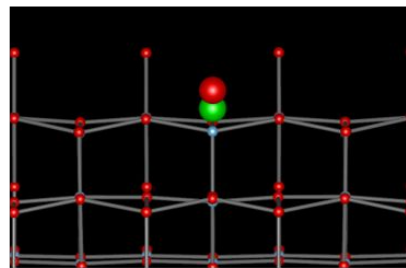
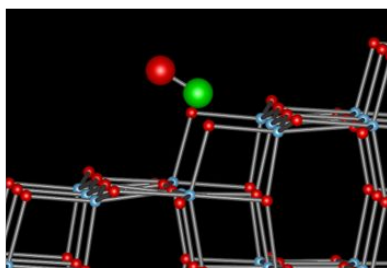
Ammonia



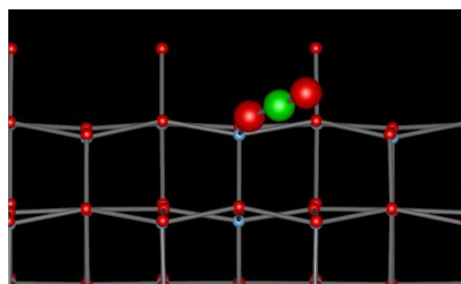
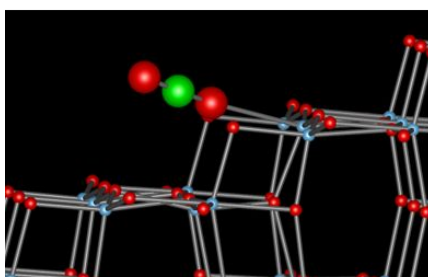
Benzene



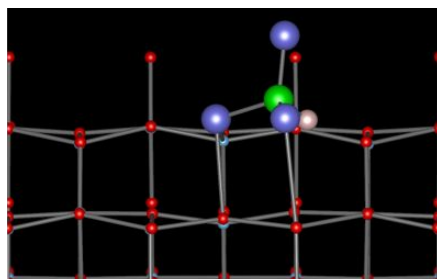
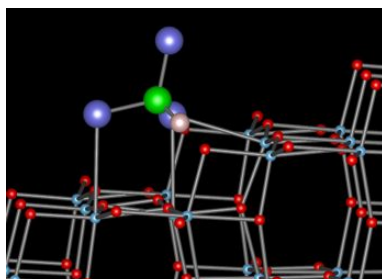
Butane



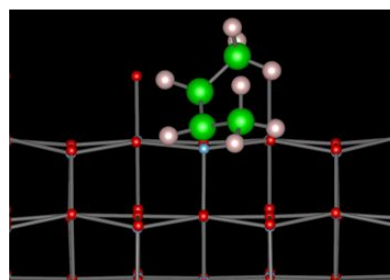
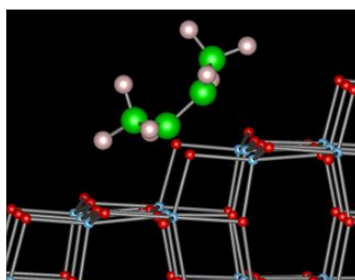
CO



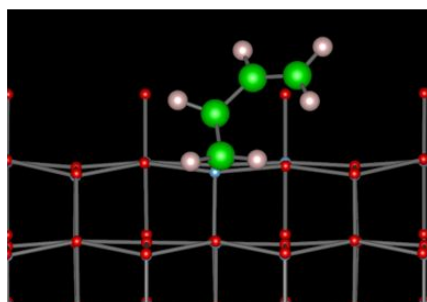
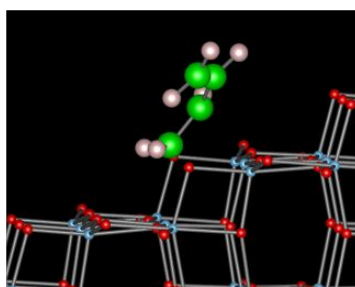
CO₂



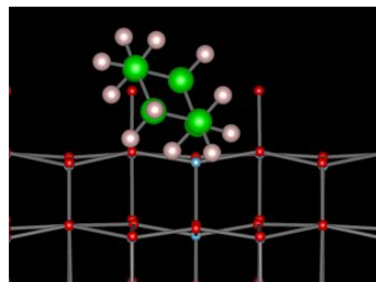
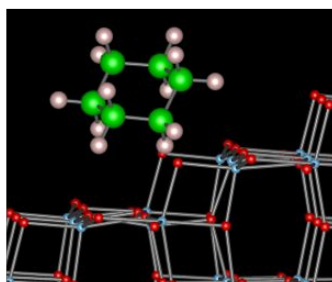
Chloroform



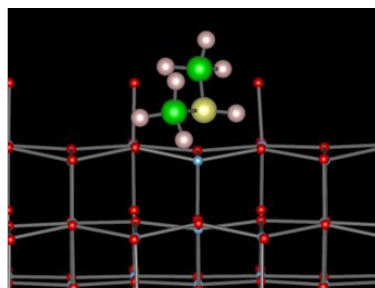
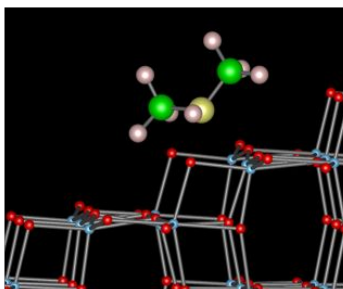
***cis*-2-Butene**



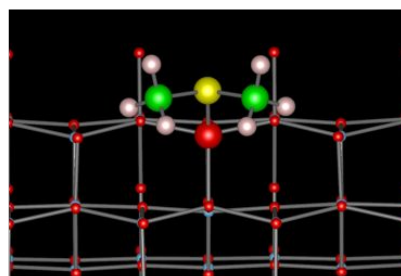
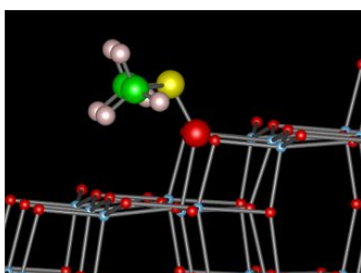
Cis-butadiene



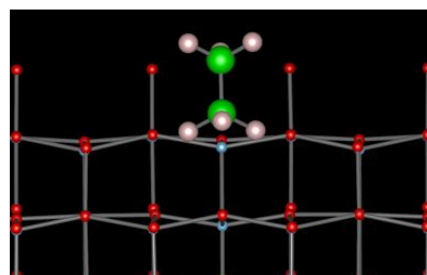
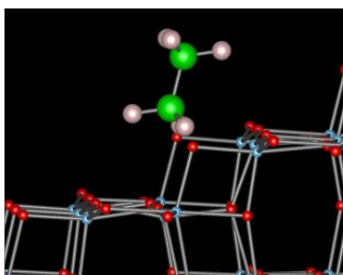
Cyclohexane



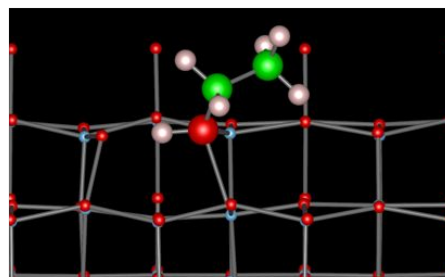
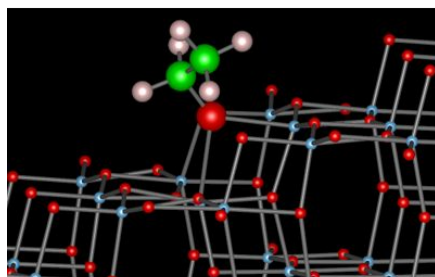
Dimethylamine



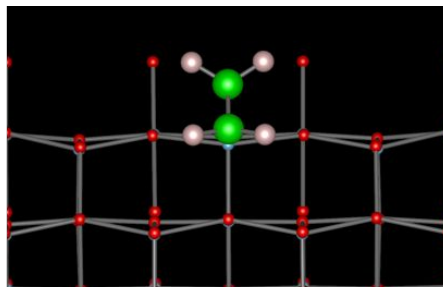
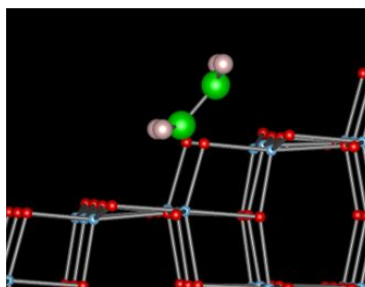
Dimethyl sulfoxide



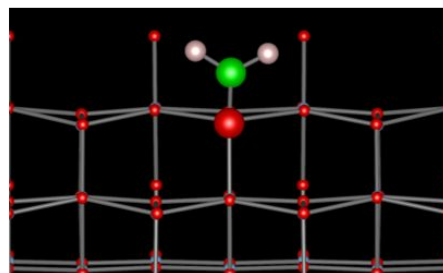
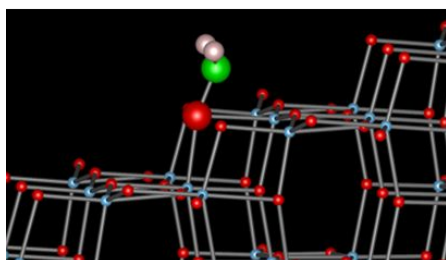
Ethane



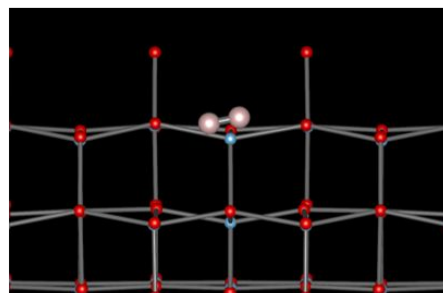
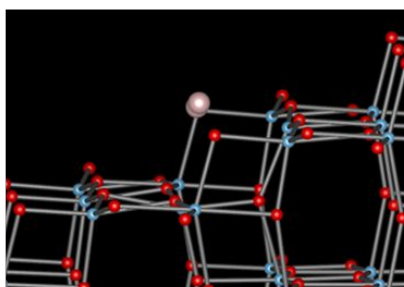
Ethanol



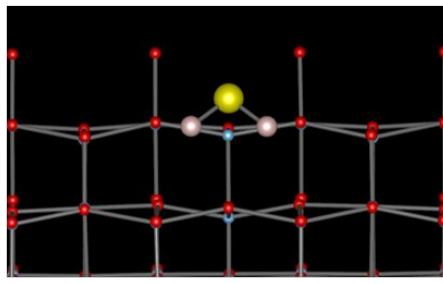
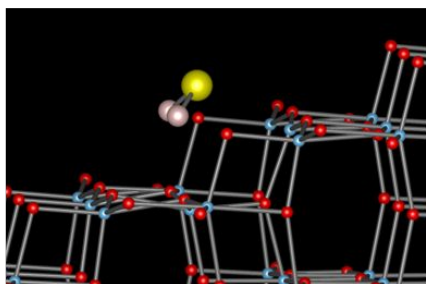
Ethylene



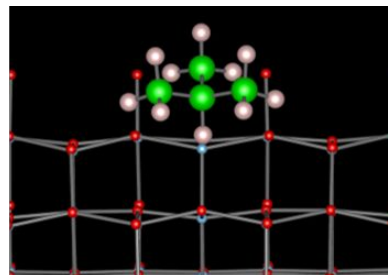
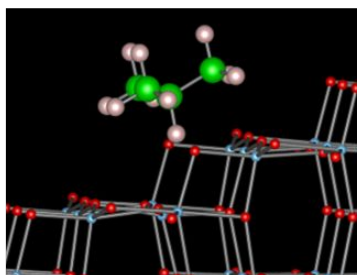
Formaldehyde



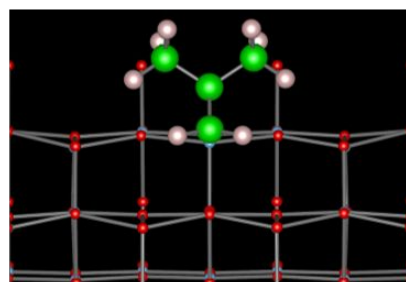
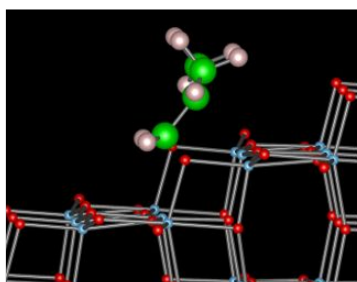
H₂



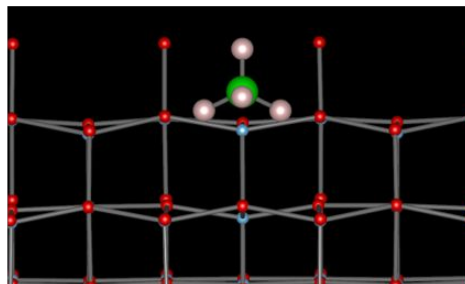
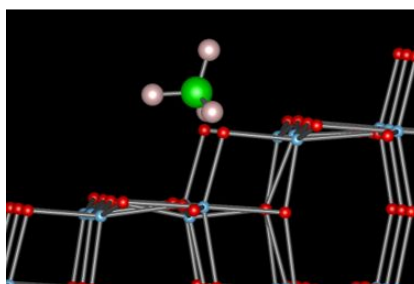
H₂S



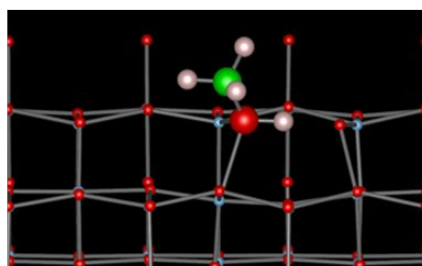
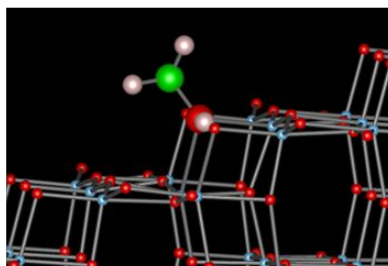
Isobutane



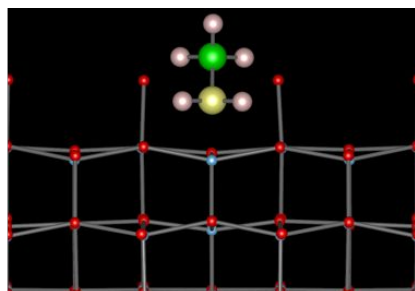
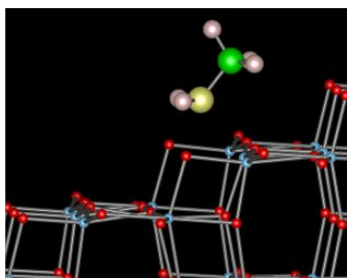
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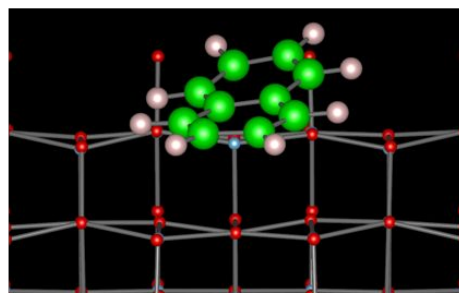
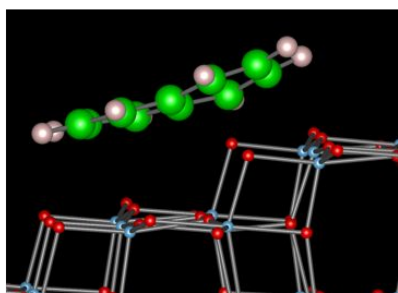
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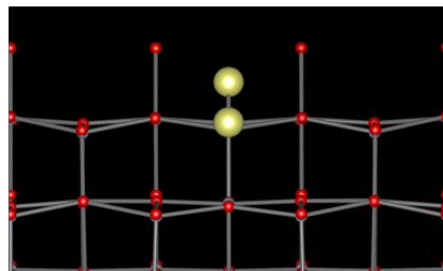
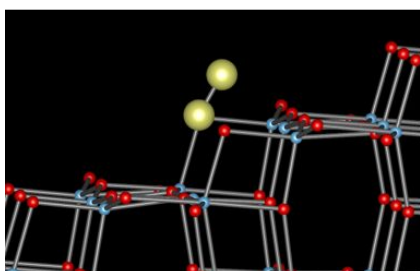
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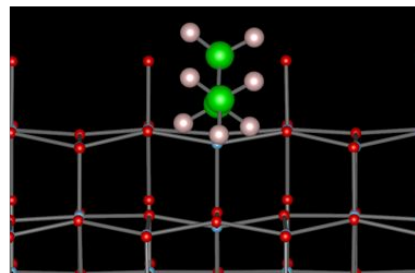
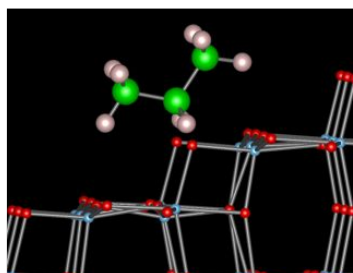
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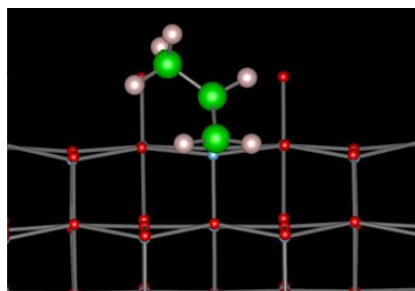
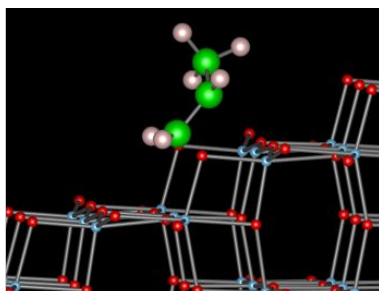
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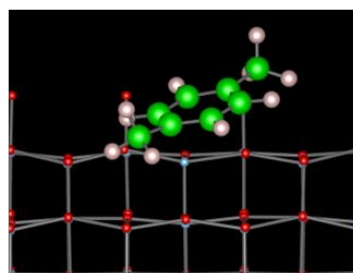
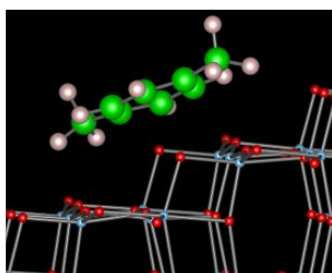
N₂



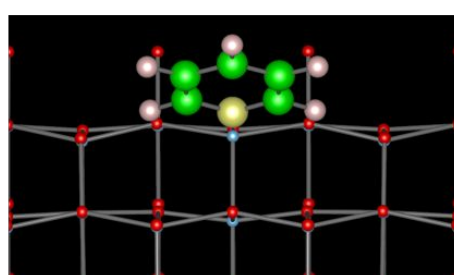
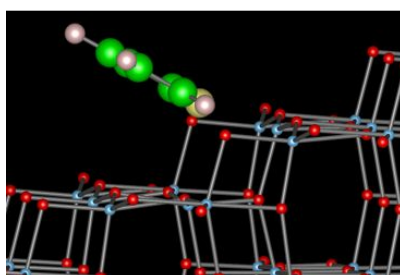
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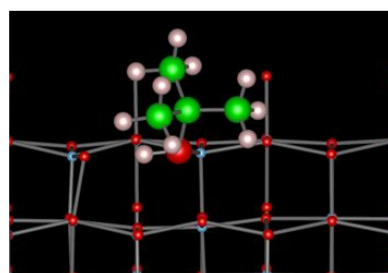
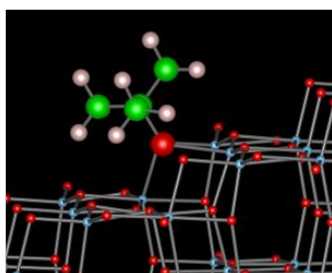
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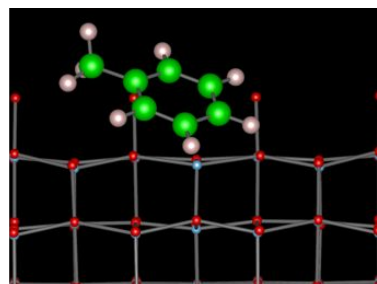
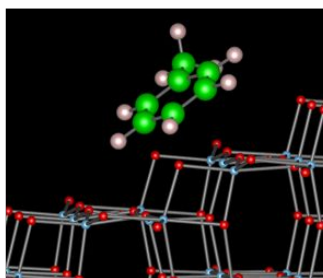
***p*-Xylene**



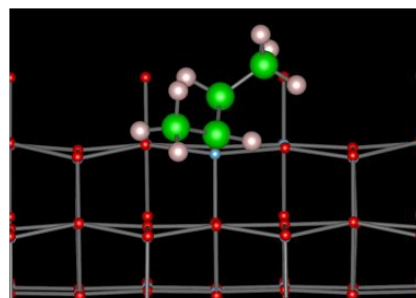
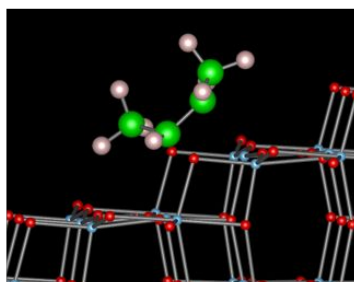
Pyridine



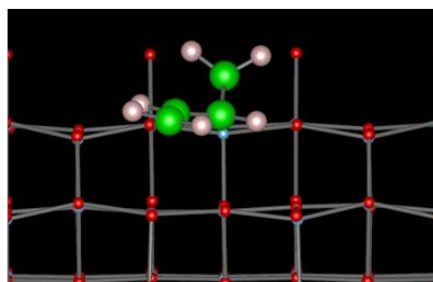
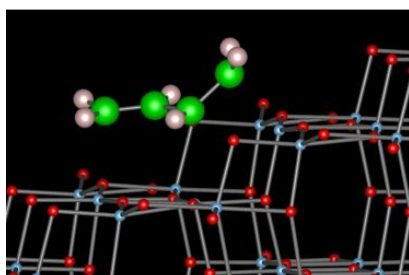
***t*-Butanol**



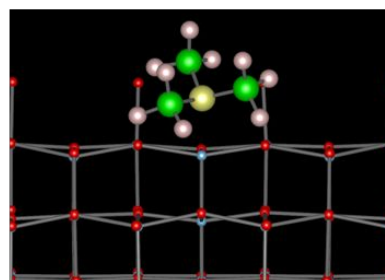
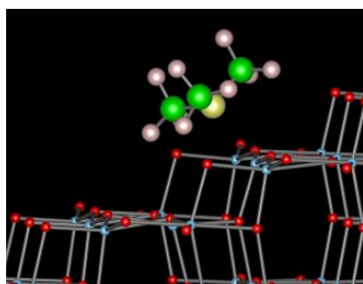
Toluene



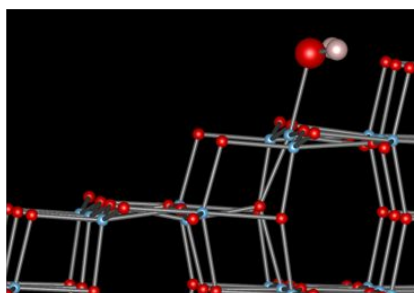
***trans*-2-Butene**



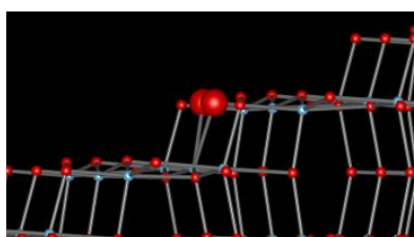
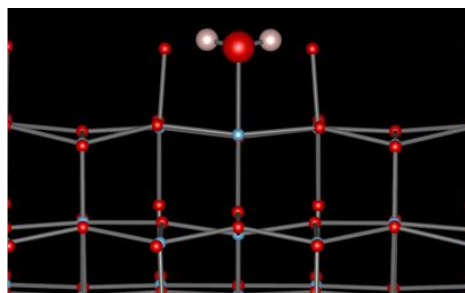
***trans*-Butadiene**



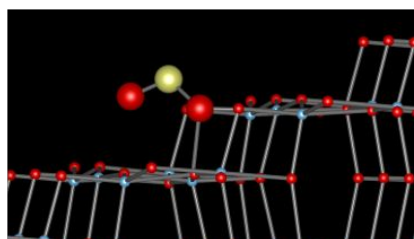
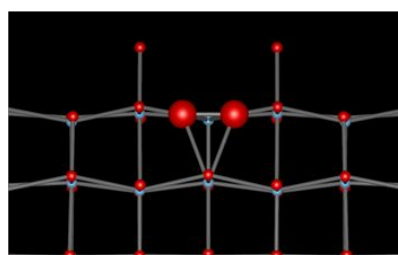
Trimethylamine



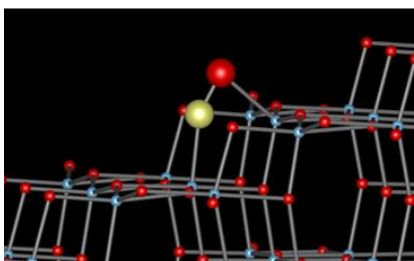
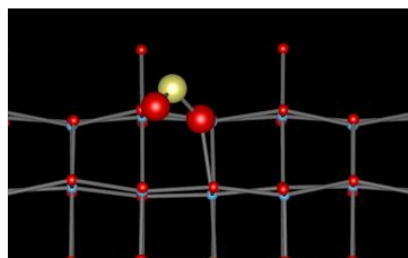
H_2O



O_2



NO_2



NO

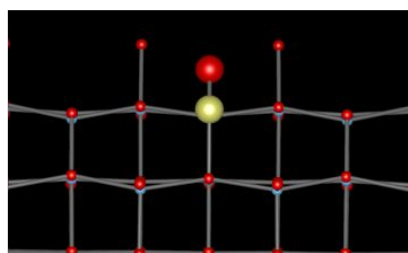
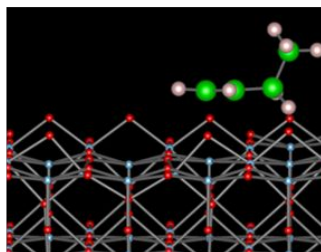
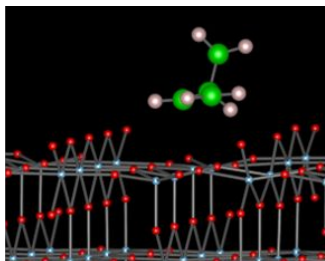
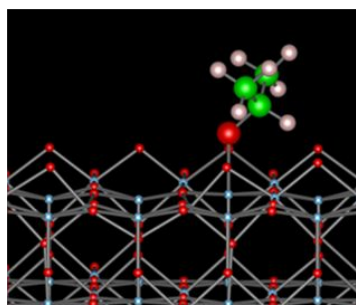
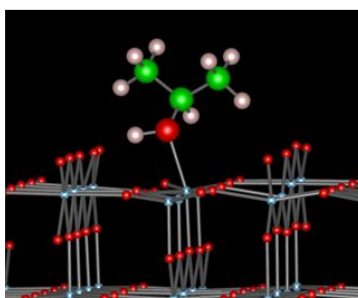


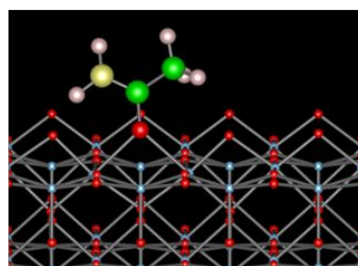
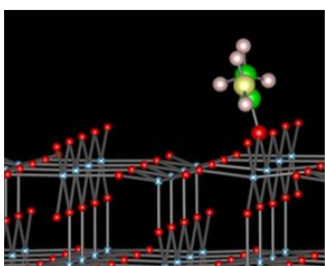
Figure S2. The most stable adsorption structures for small molecules on the anatase (101) surface with an oxygen vacancy.



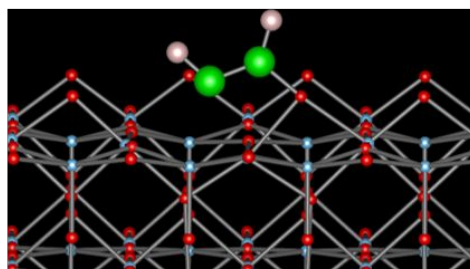
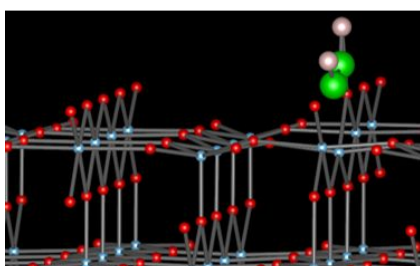
1-Butene



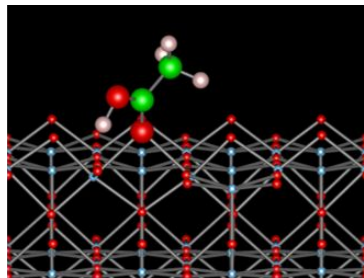
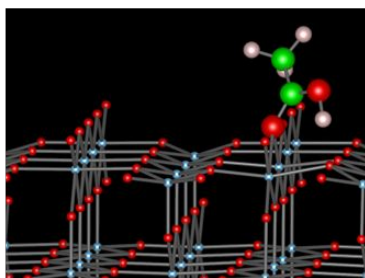
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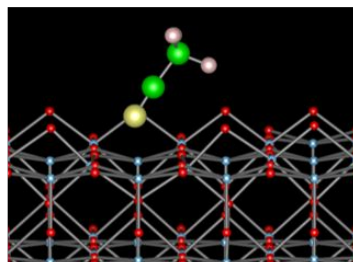
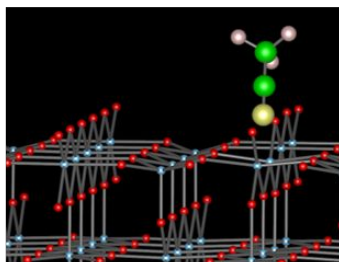
Acetamide



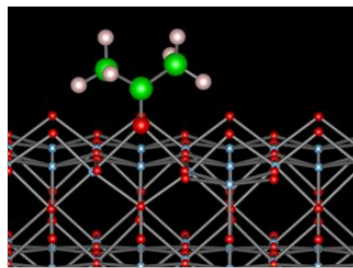
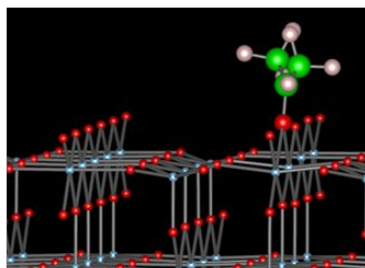
Acetylene



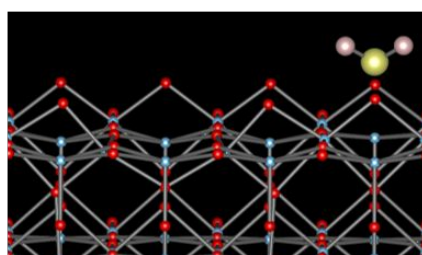
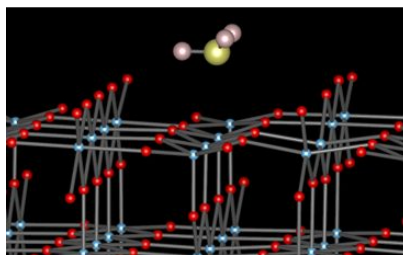
Acetic acid



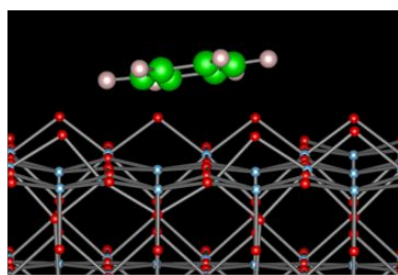
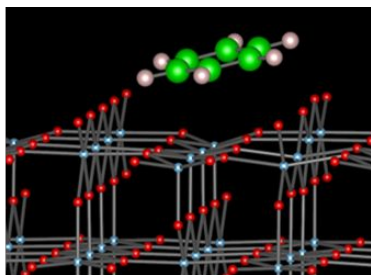
Acetonitrile



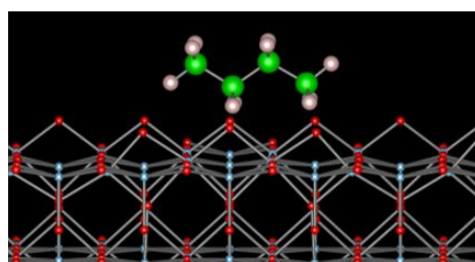
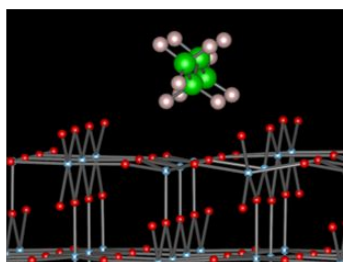
Acetone



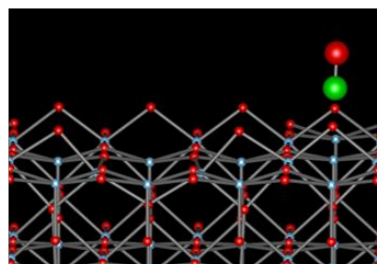
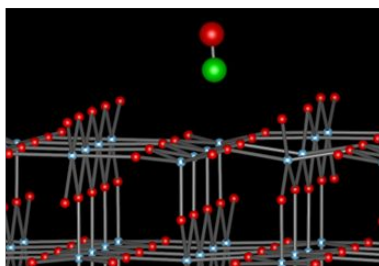
Ammonia



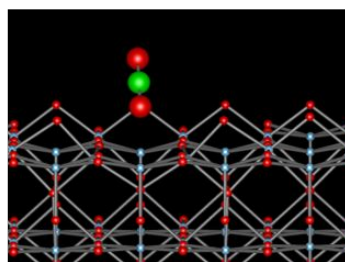
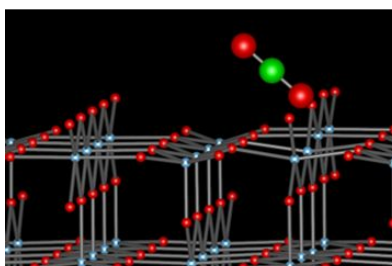
Benzene



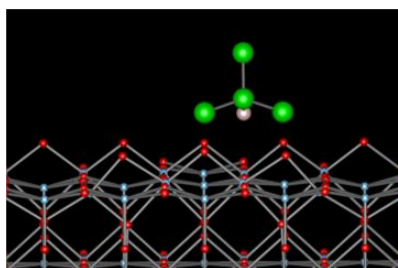
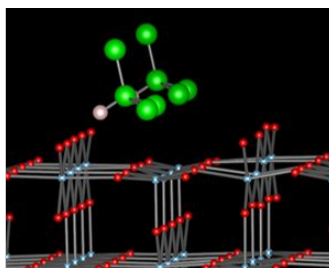
Butane



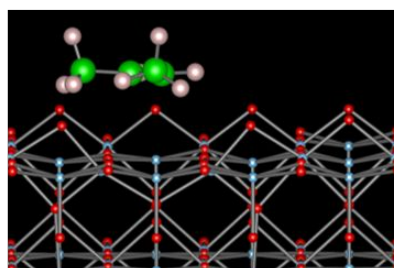
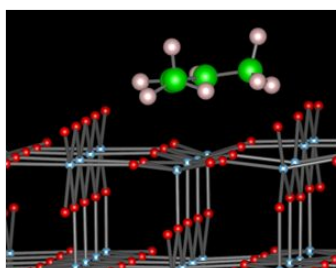
CO



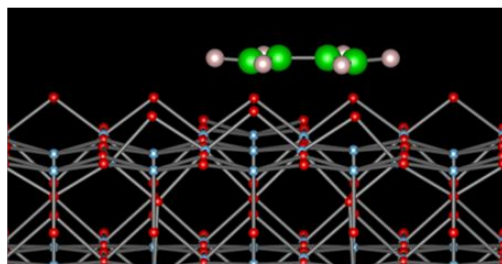
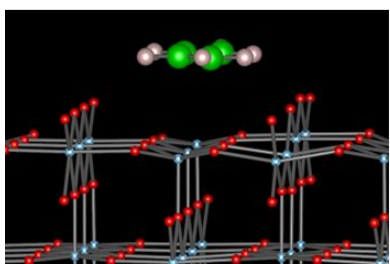
CO₂



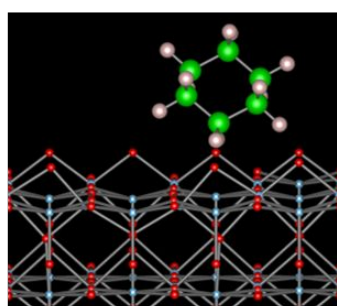
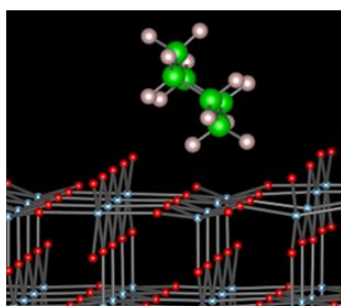
Chloroform



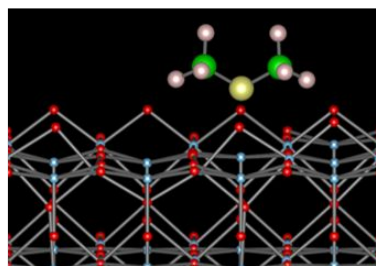
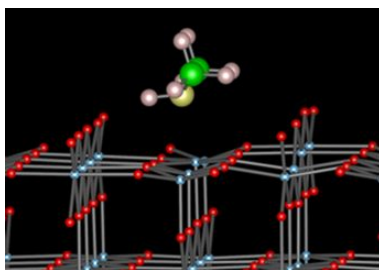
***cis*-2-Butene**



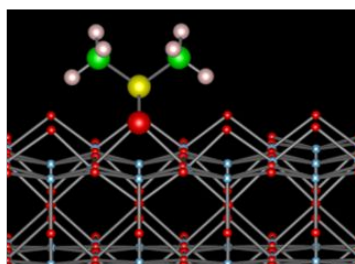
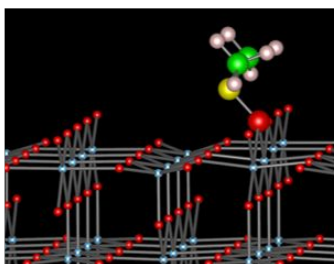
***cis*-Butadiene**



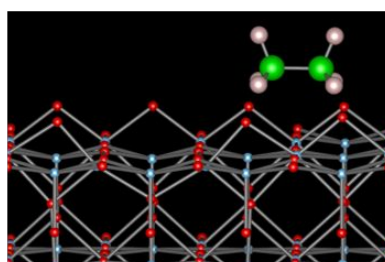
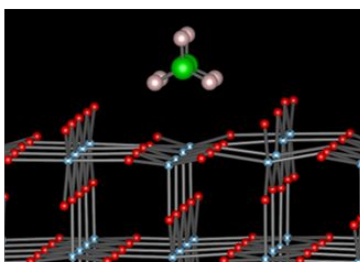
Cyclohexane



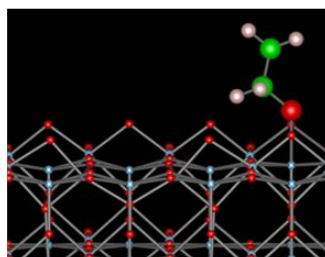
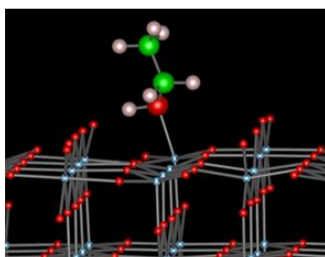
Dimethylamine



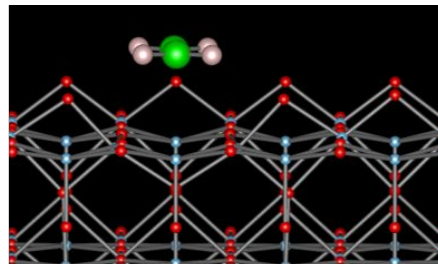
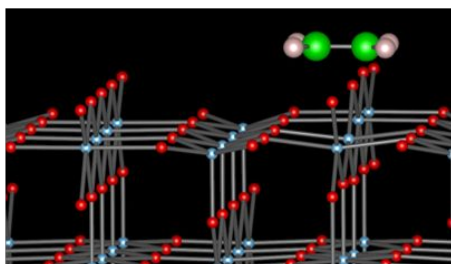
Dimethyl sulfoxide



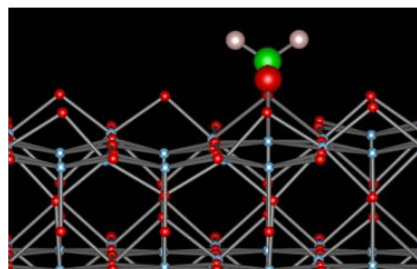
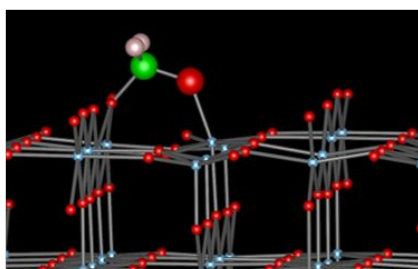
Ethane



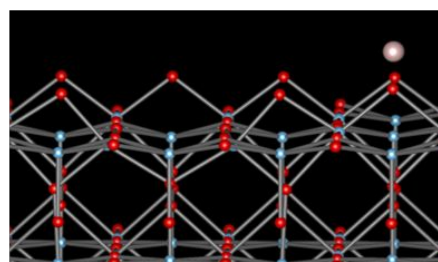
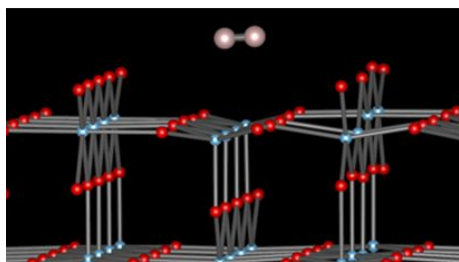
Ethanol



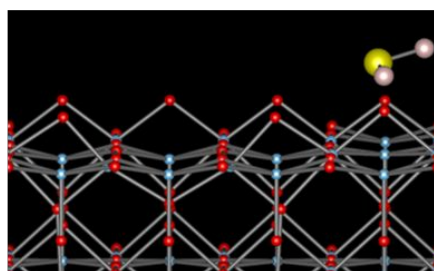
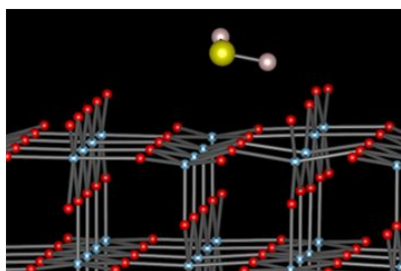
Ethylene



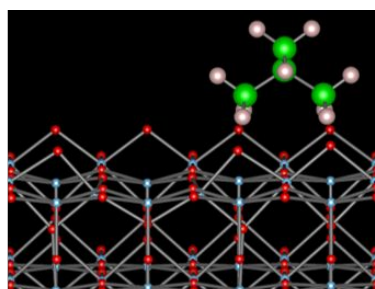
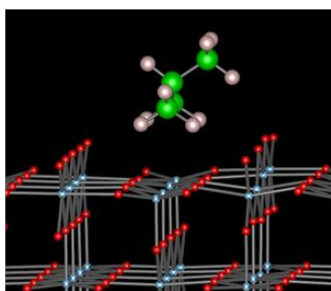
Formaldehyde



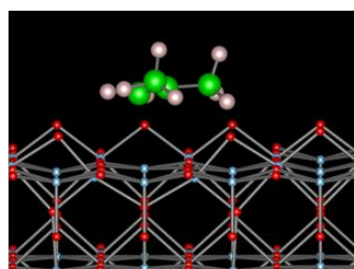
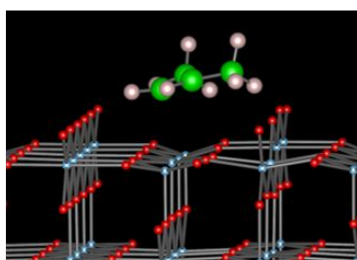
H₂



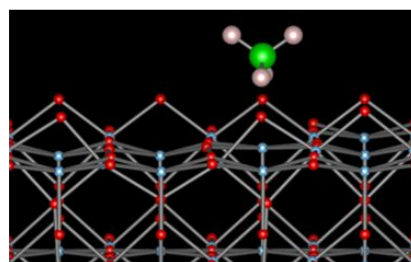
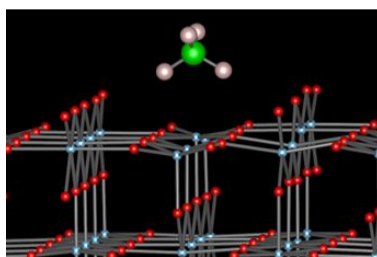
H₂S



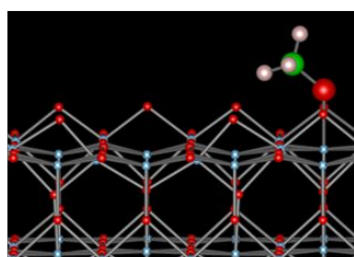
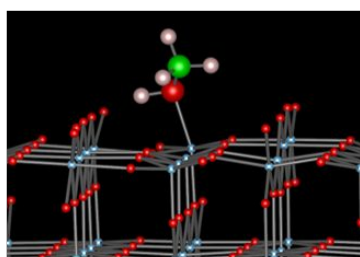
Isobutane



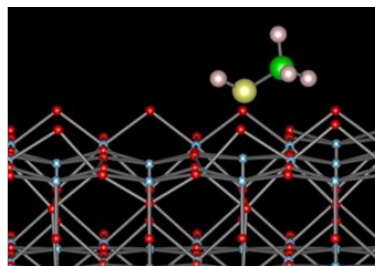
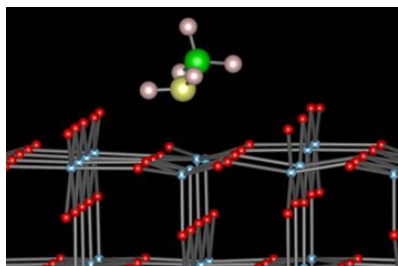
Isobutene



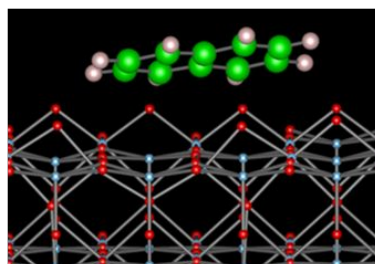
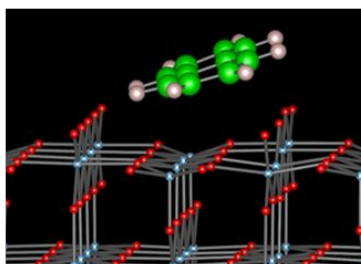
Methane



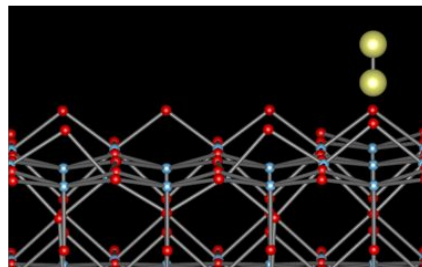
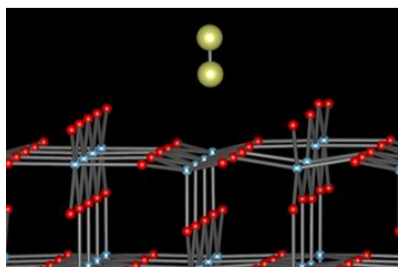
Methanol



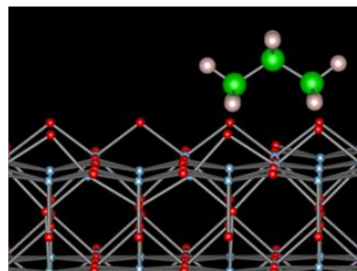
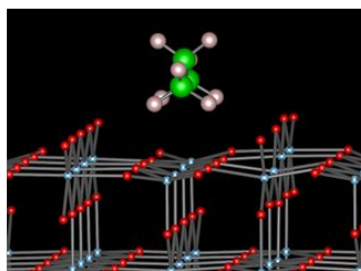
Methylamine



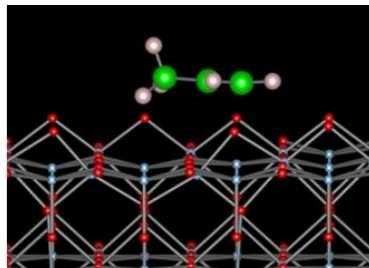
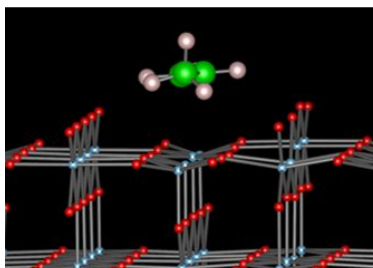
Naphthalene



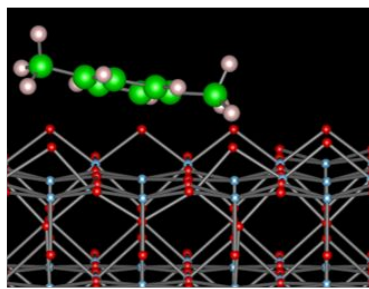
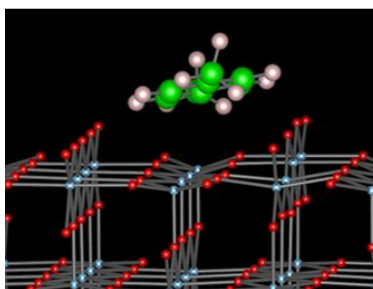
N₂



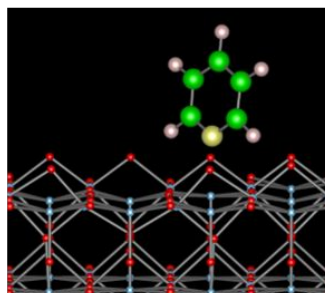
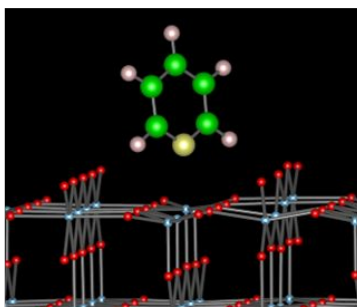
Propane



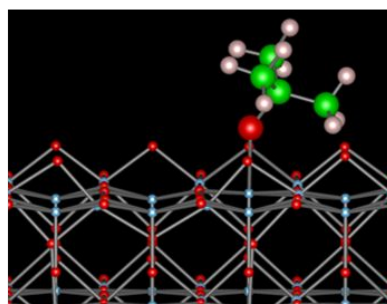
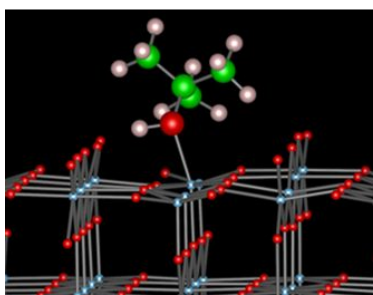
Propylene



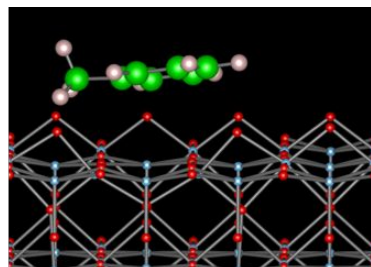
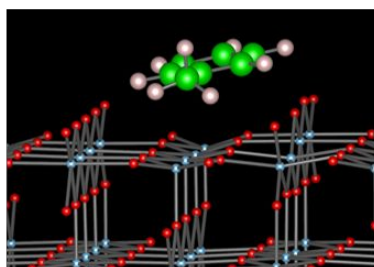
***p*-Xylene**



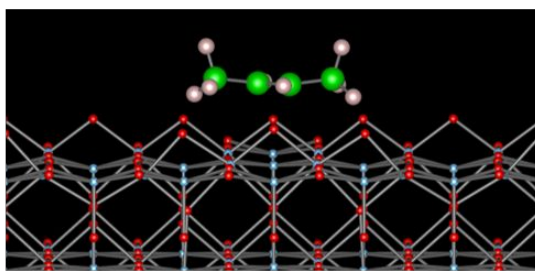
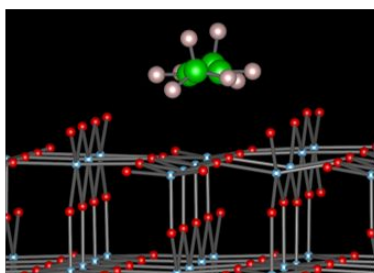
Pyridine



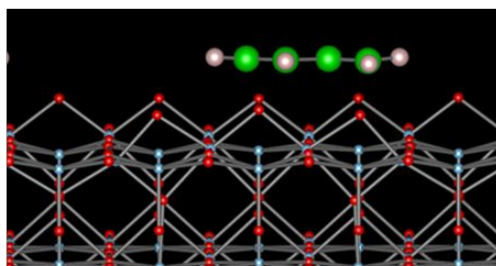
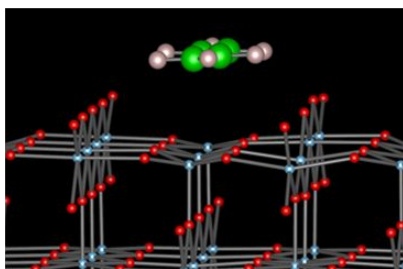
***t*-Butanol**



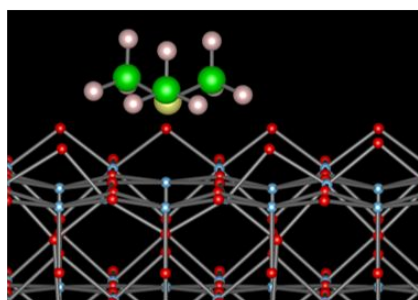
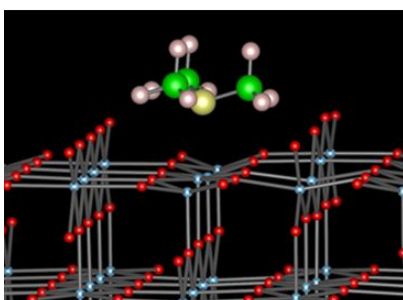
Toluene



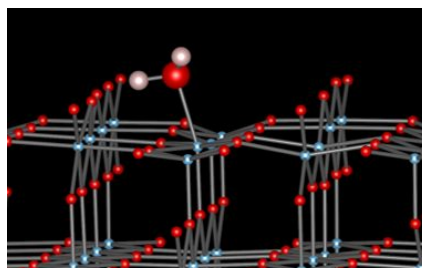
***trans*-2-Butene**



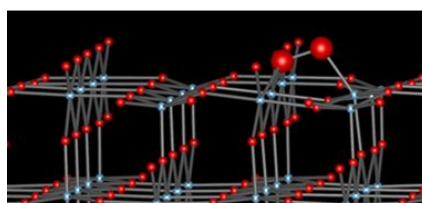
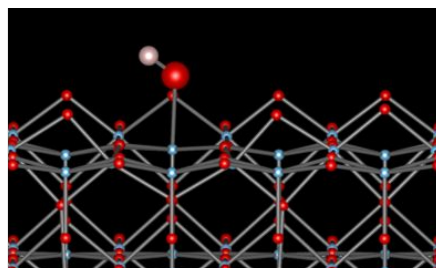
***trans*-Butadiene**



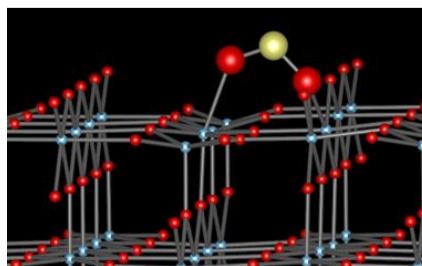
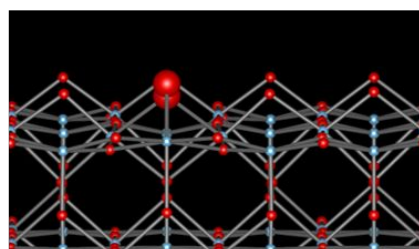
Trimethylamine



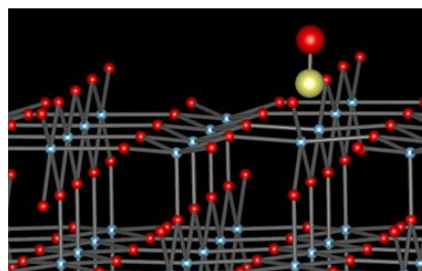
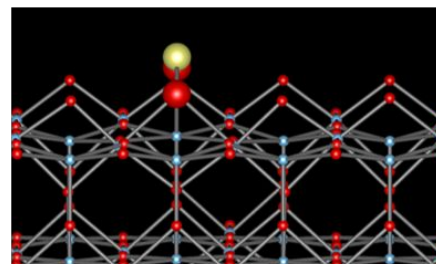
H₂O



O₂



NO₂



NO

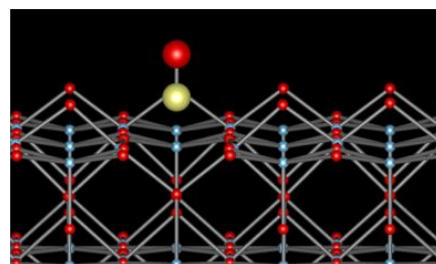
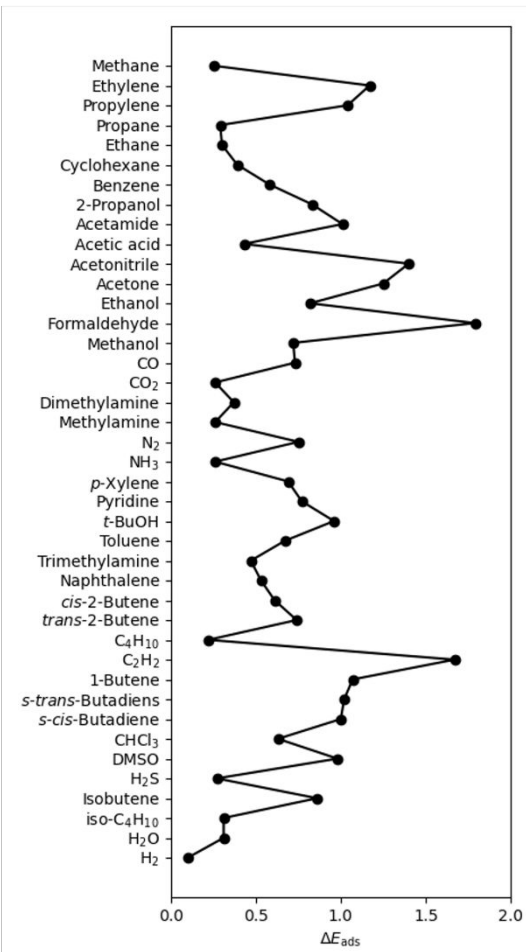


Figure S3. The most stable adsorption structures for small molecules on the rutile (110) surface with an oxygen vacancy.

(a) anatase



(b) rutile

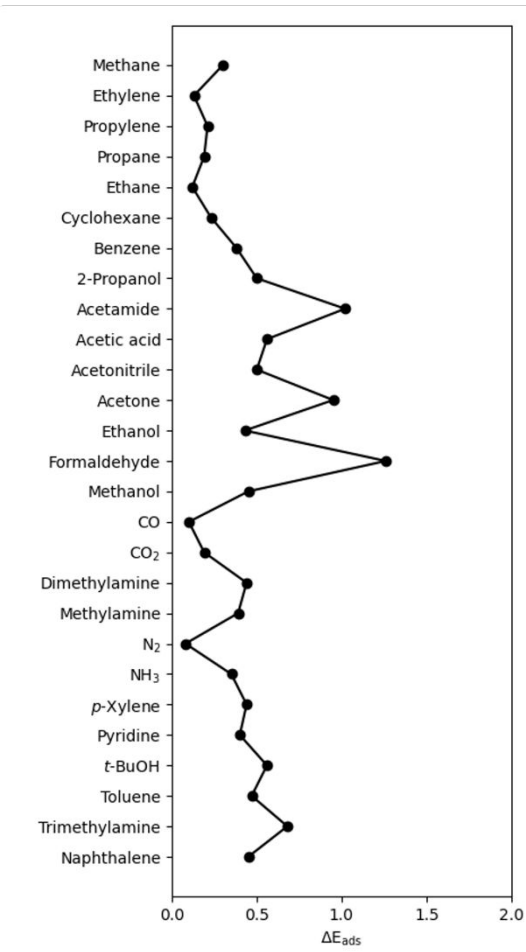


Figure S4. Difference in computed adsorption energy for small molecules between pristine and defective surfaces.

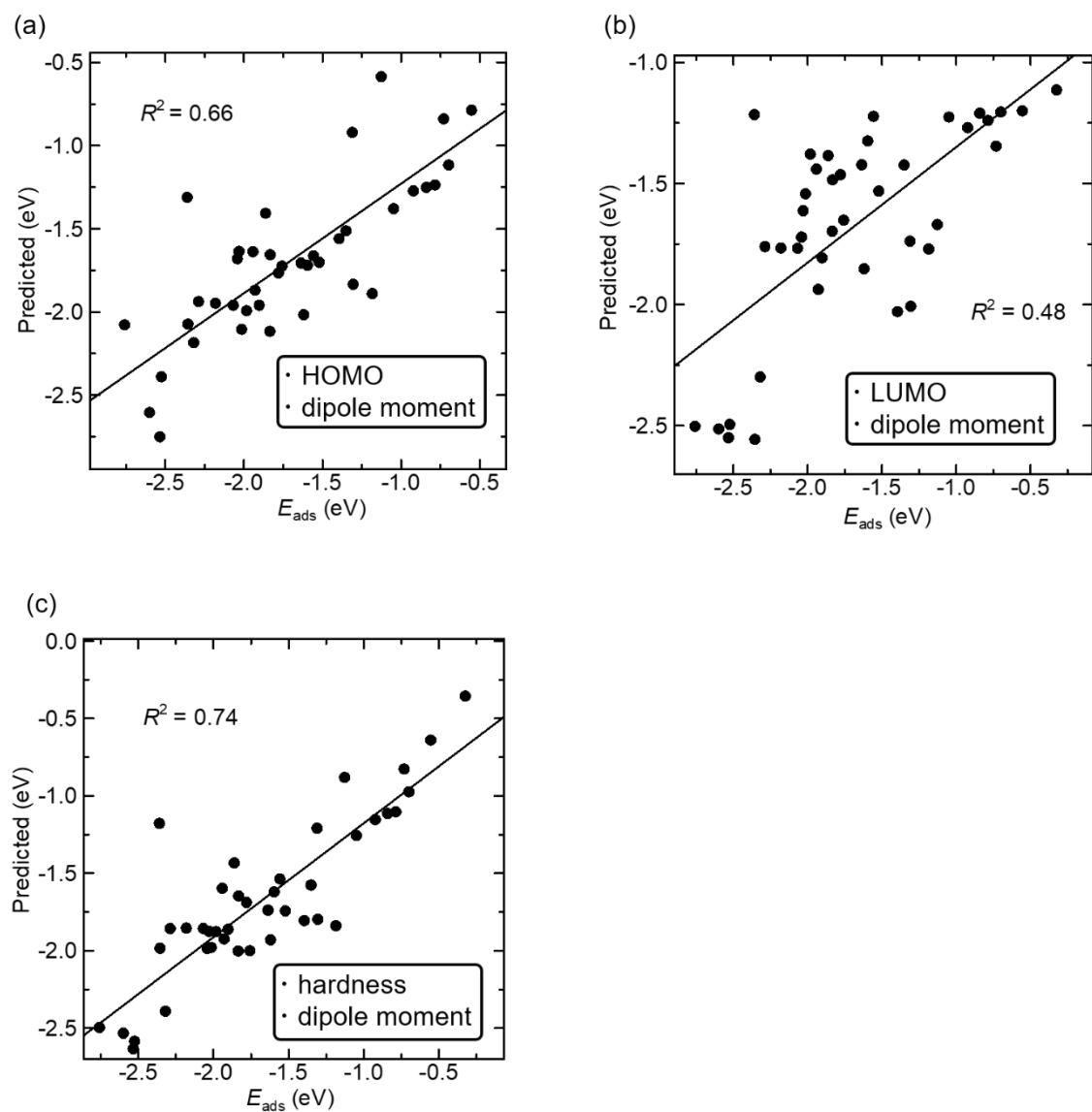


Figure S5. E_{ads} of molecular groups without radical molecules on an anatase (101) surface and the predicted values obtained using the MLR methods.

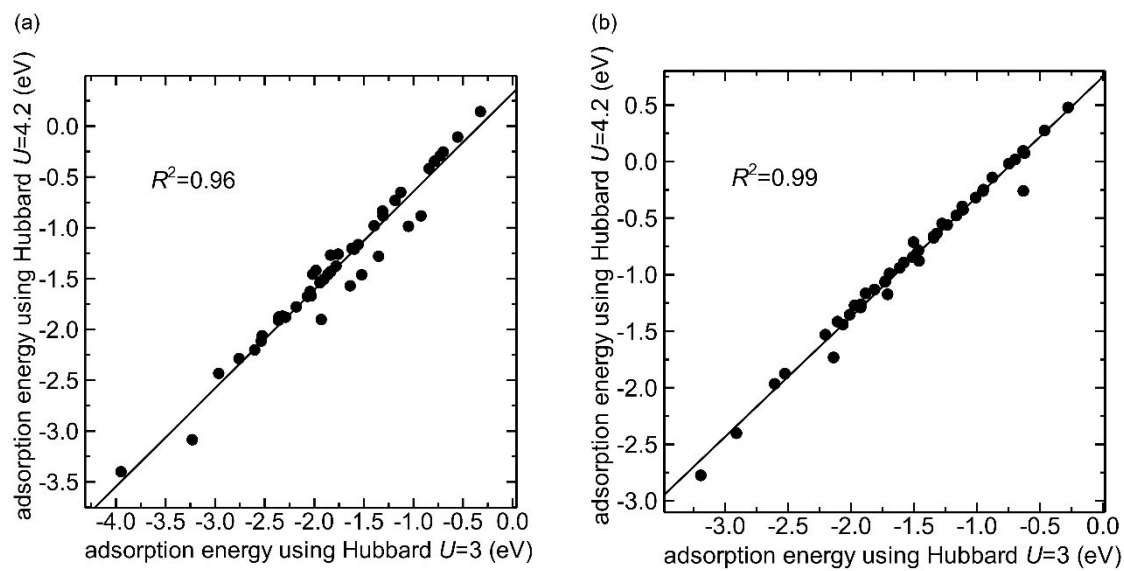


Figure S6. Correlation of the adsorption energy between $U=3$ and $U=4.2$. (a) anatase surface and (b) rutile one.