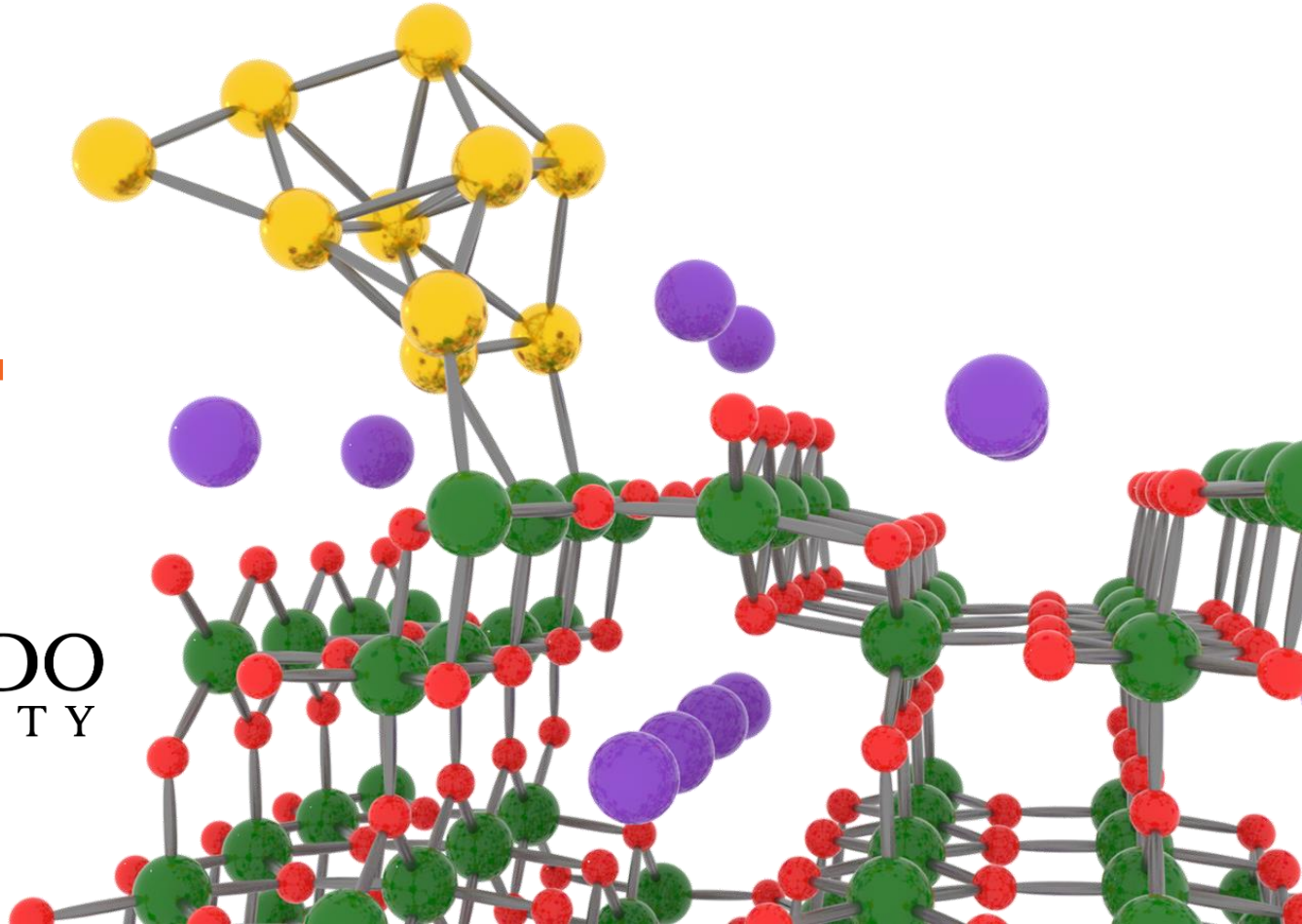
# DFT Mechanistic Study on the Heterogeneous Gold Catalysis: the Role of the Support Material for the C–H Bond Activation

**Ray Miyazaki**

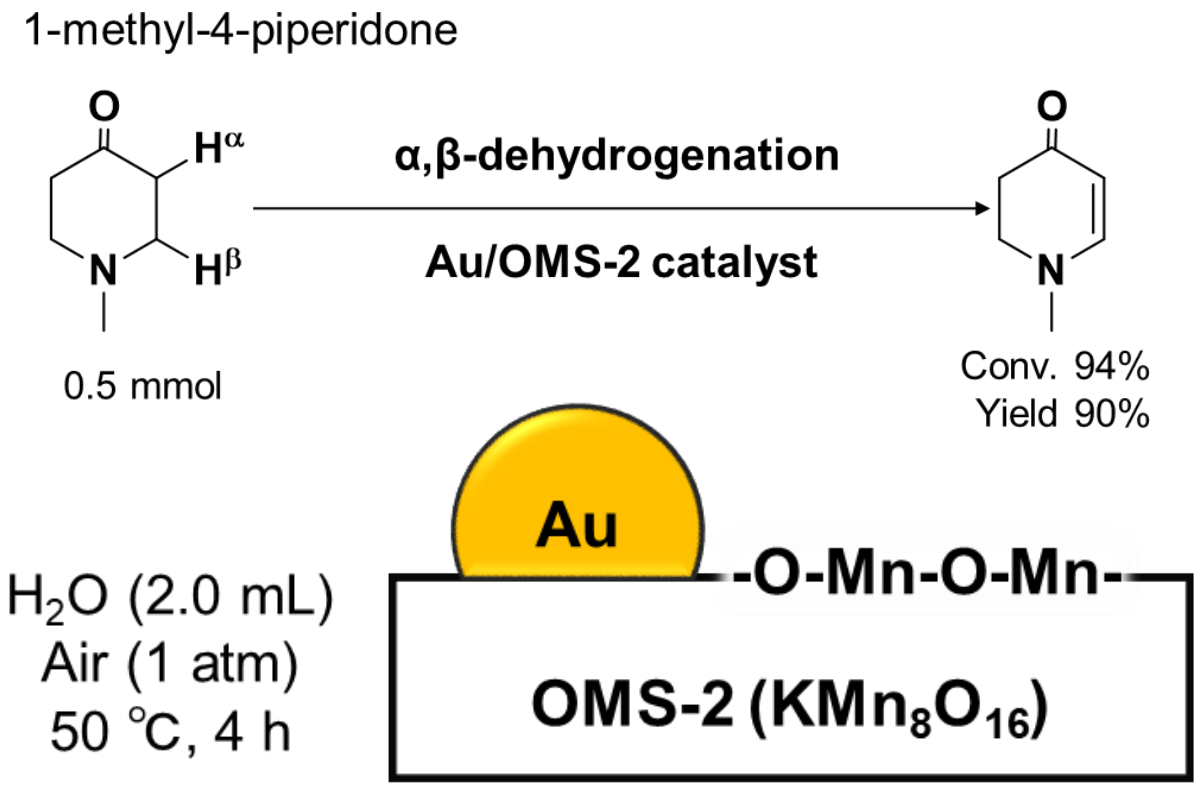
*Coffee Talk Oct. 4th, 2021*



Institute for Catalysis
ICAT

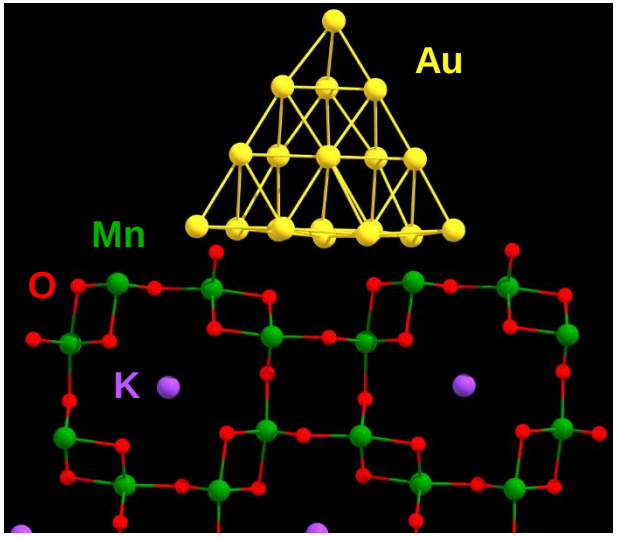
HOKKAIDO UNIVERSITY

**Au nanoparticles supported on OMS-2 support (Au/OMS-2 catalyst) catalyze α, β-dehydrogenation of 1-methyl-4-piperidone [1].**



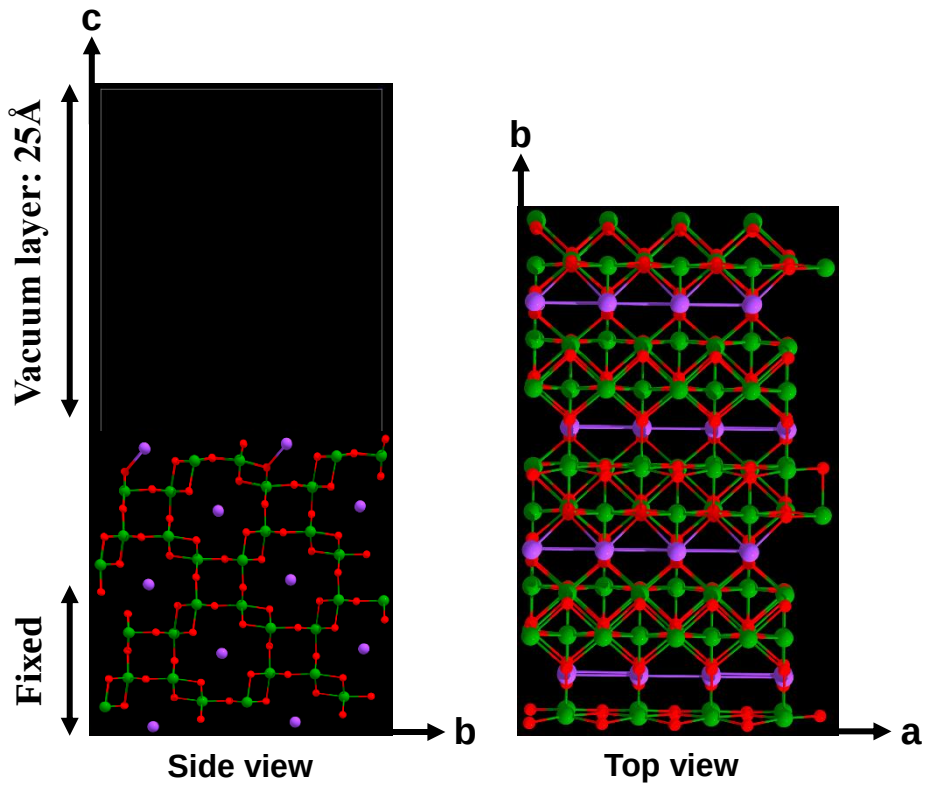

**Reaction mechanism of the Au/OMS-2 catalyst is investigated by theoretical calculation.**

[1] D. Yoshii, X. Jin, T. Yatabe, J. Hasegawa, K. Yamaguchi, and N. Mizuno, *Chem. Commun*. 52, 14314-14317, (2016)




**OMS-2 ($KMn_8O_{16}$)**

To investigate electronic structure of Au on OMS-2 support, periodic slab model of the OMS-2 surface was constructed.




## Computational Details for the Slab Model

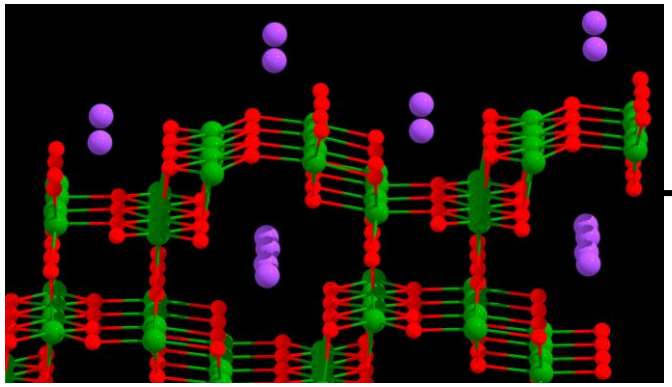
Model: 4x2x2 super cell of OMS-2
(a = 11.47 Å, b = 19.61 Å, c = 19.61 Å (+25 Å))

Method: Density Functional Theory [DFT]
Functional: PBE
Basis set: Geometry Optimization: Light_default
Energy Calculation: Tight_default
("cut_pot" for K is set to 4.0 Å)
k-grid: 18x6x6 for bulk model
5x3x1 for slab model
Relativistic: Atomic ZORA approximation
Charge: neutral
Spin: collinear

Program: FHI-aims (version: 171221)

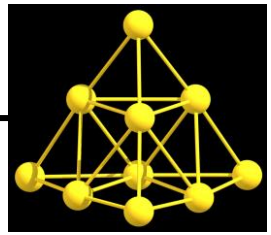
FHI-aims
The ab initio materials simulation package

$Au_{10}$ model was supported on the slab model of OMS-2 surface ($Au_{10}$/OMS-2 model) as a computational model of the Au/OMS-2 catalyst.



Slab model of OMS-2

Geometry Optimization

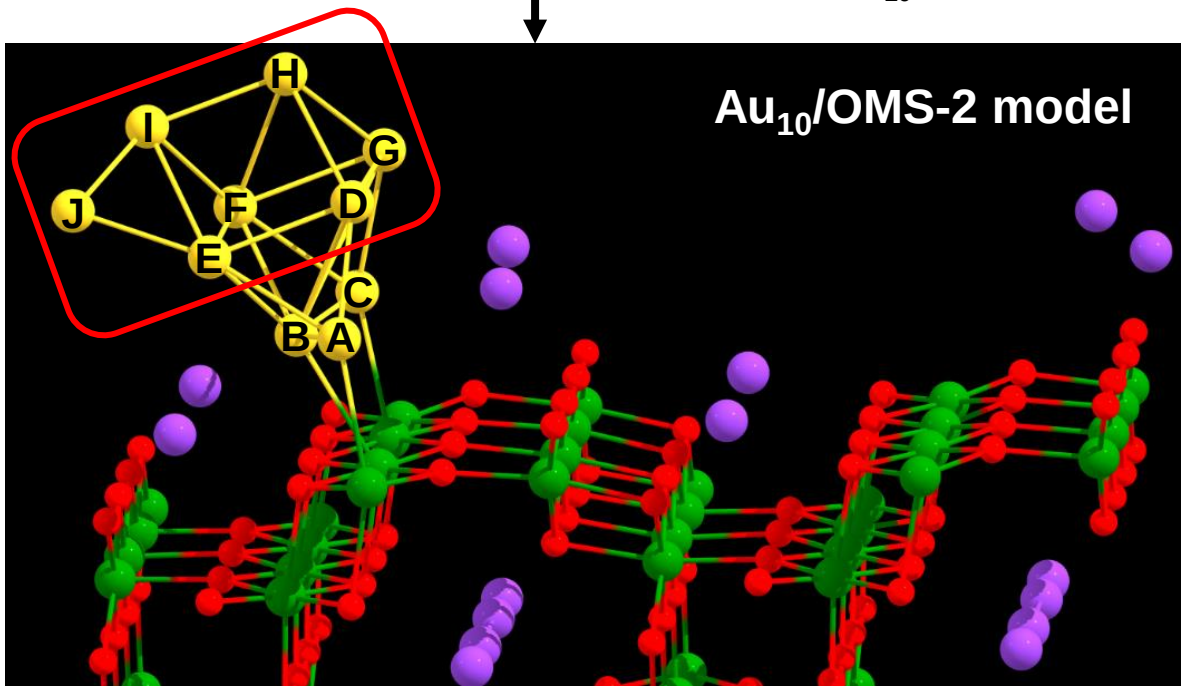


$Au_{10}$ model

**Hirshfeld Charge**

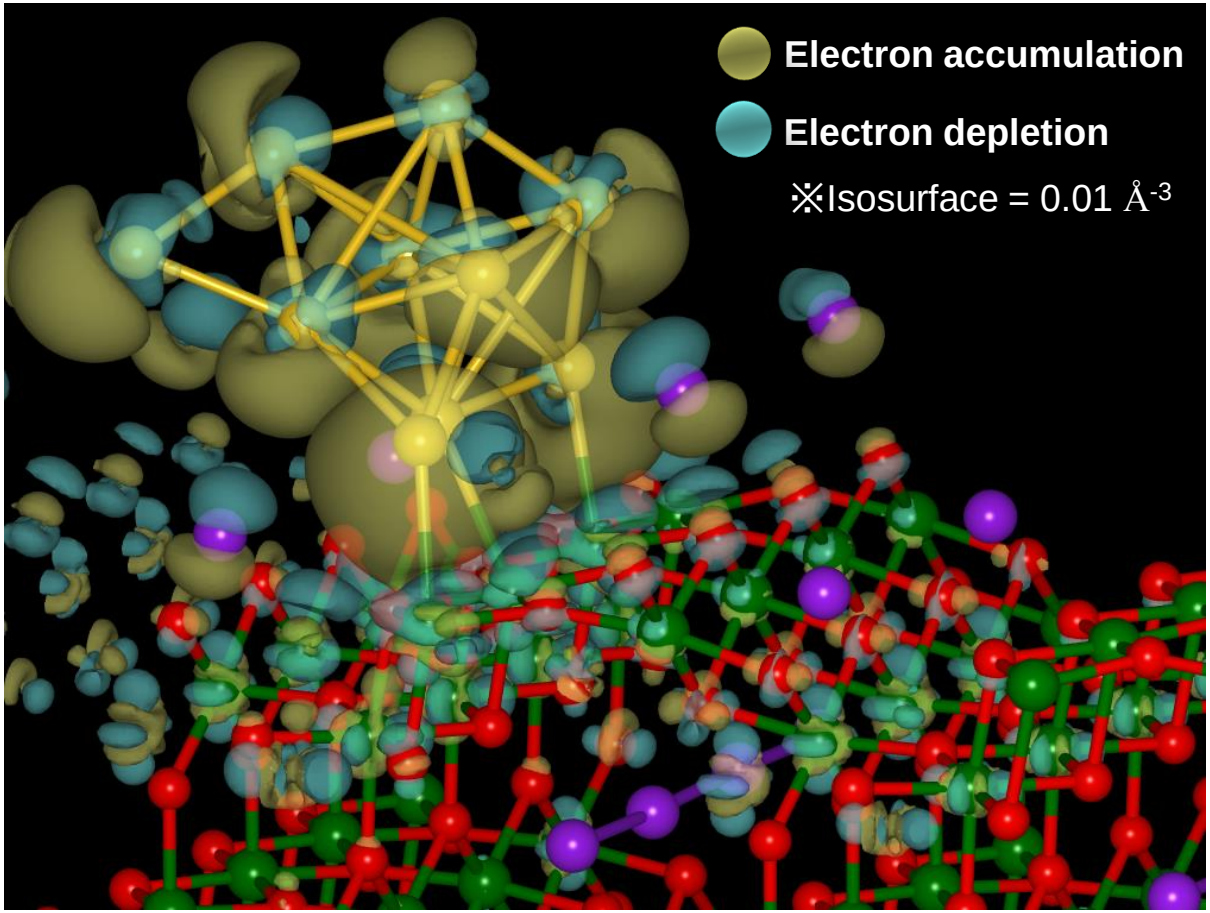
| | |
|---|---|
| $Au^A$: | 0.00 |
| $Au^B$: | 0.13 |
| $Au^C$: | 0.02 |
| $Au^D$: | -0.06 |
| $Au^E$: | 0.01 |
| $Au^F$: | -0.06 |
| $Au^G$: | -0.13 |
| $Au^H$: | -0.09 |
| $Au^I$: | -0.09 |
| $Au^J$: | -0.15 |

**$Au_{10}$: -0.42**




**It was suggested that Au cluster on the OMS-2 surface is negatively charged.**

To investigate the difference of electron density induced by the interaction between Au and OMS-2, electron density difference analysis was performed.

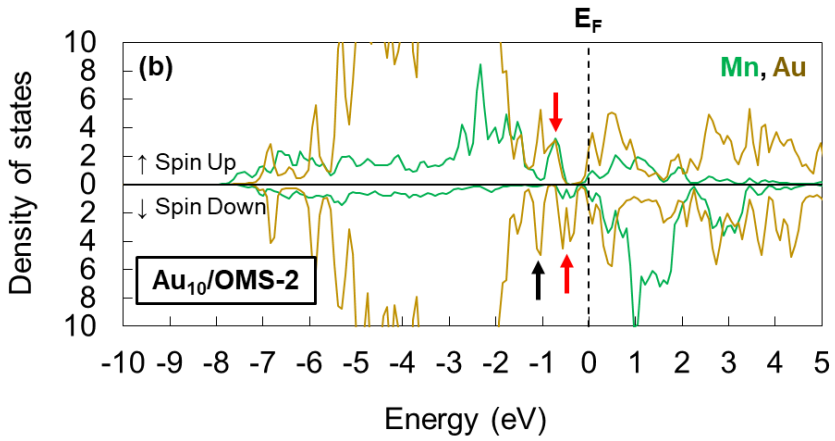


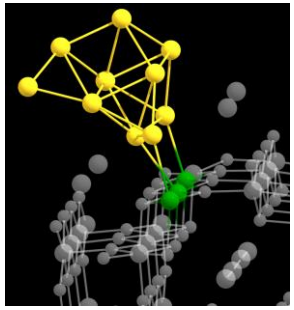

**・Electron density around Au-Mn bond and Au atoms on the 2nd and 3rd layers of Au cluster are increased ↔ Good agreement with the result of Hirshfeld charge analysis.**

**・Electron density around Mn atoms and O atoms on the OMS-2 surface are decreased.**

**⇒Charge transfer from OMS-2 to Au was suggested.**

Next, atom projected density of states (p-DOS) of the $Au_{10}$/OMS-2 model was calculated.



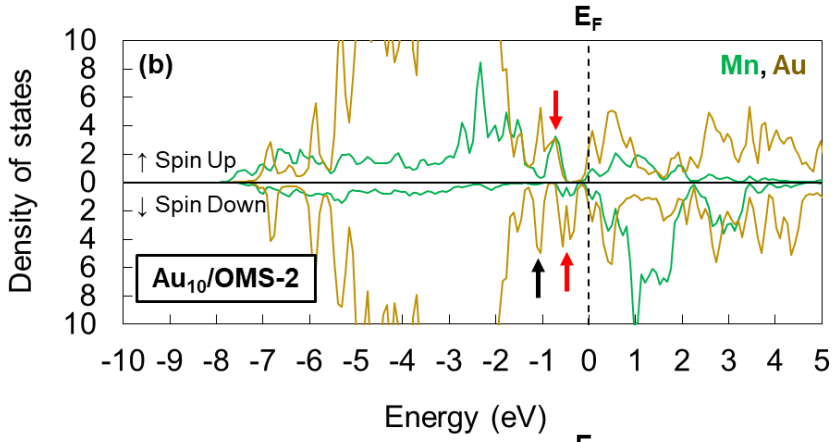
**$Au_{10}$/OMS-2 model**

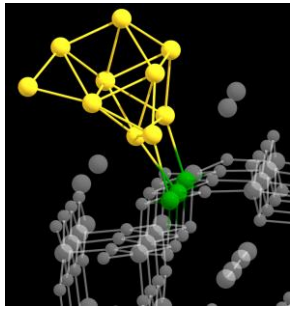
**Yellow: Total-DOS projected to the $Au_{10}$ region.**

**Green: Total-DOS projected to Mn atoms which are directly bonded to the $Au_{10}$ model.**

**Energy revels of Au and Mn are well overlapped around the valence band near Fermi level.**

Next, atom projected density of states (p-DOS) of the $Au_{10}$/OMS-2 model was calculated.



**$Au_{10}$/OMS-2 model**

**Yellow: Total-DOS projected to the $Au_{10}$ region.**

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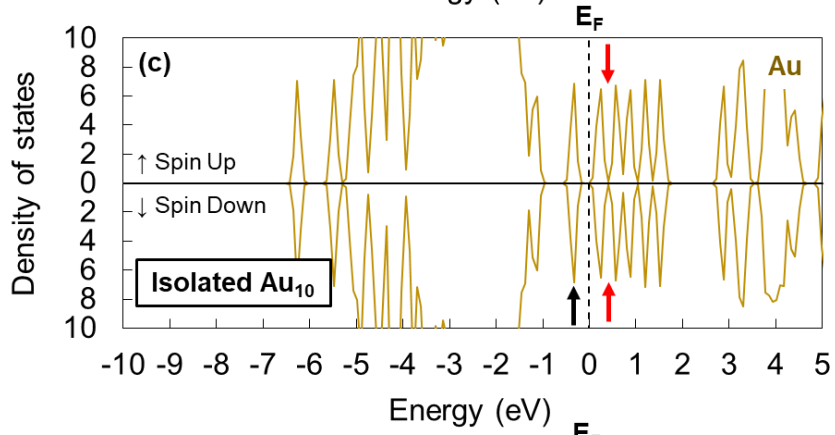
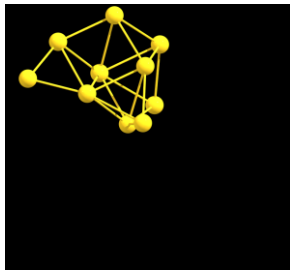
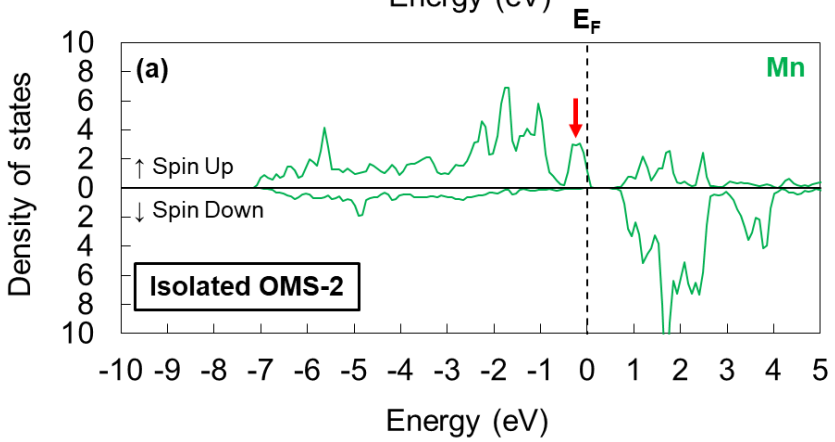
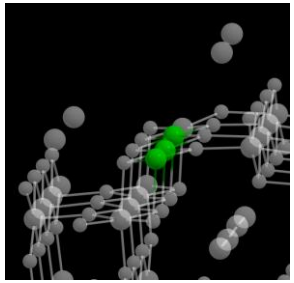


**Isolated $Au_{10}$ model taken from the $Au_{10}$/OMS-2 model**

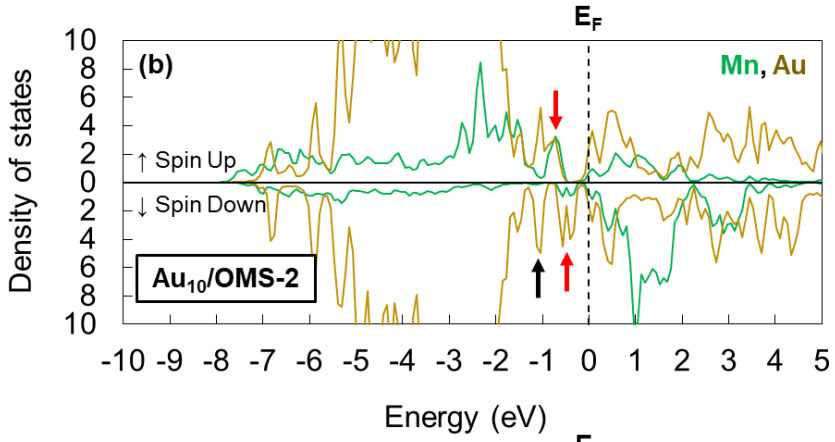
**Yellow: Total-DOS of the $Au_{10}$ model.**

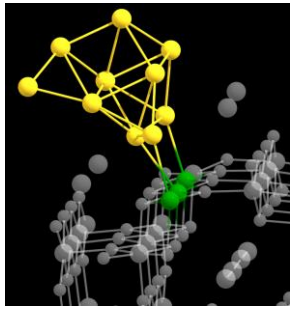


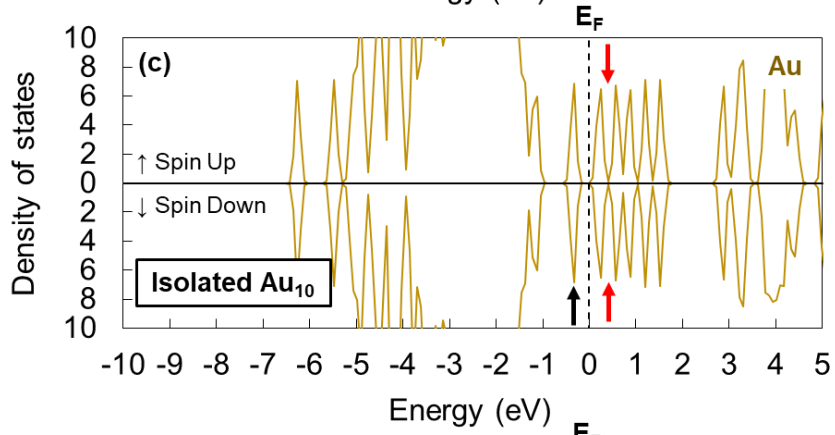
**Isolated OMS-2 model taken from the $Au_{10}$/OMS-2 model**

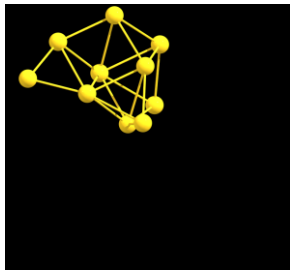
**Green: Total-DOS projected to Mn atoms which were directly bonded to the $Au_{10}$ model.**



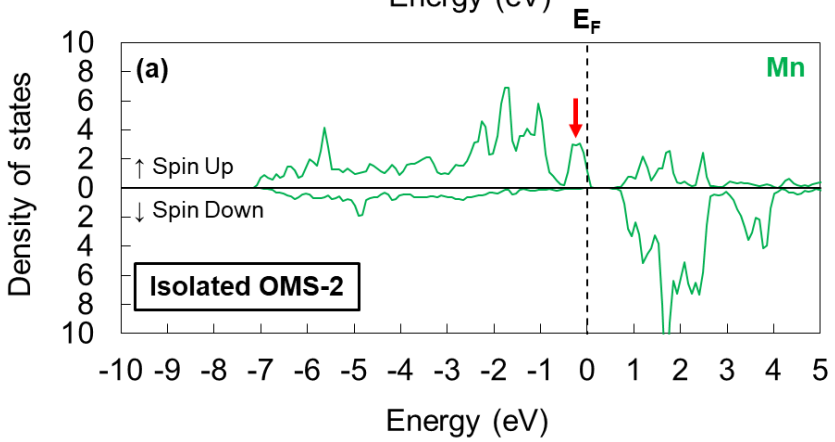



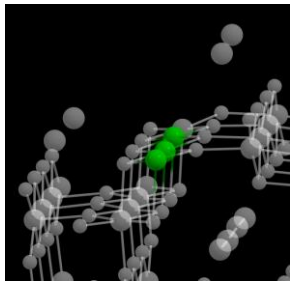
It was suggested that **valence electrons of the OMS-2 surface were transferred to the Au cluster to form the Au-Mn bonds**.



- Unfilled bands of isolated $Au_{10}$ model were shifted below the Fermi level in the $Au_{10}$/OMS-2 model.

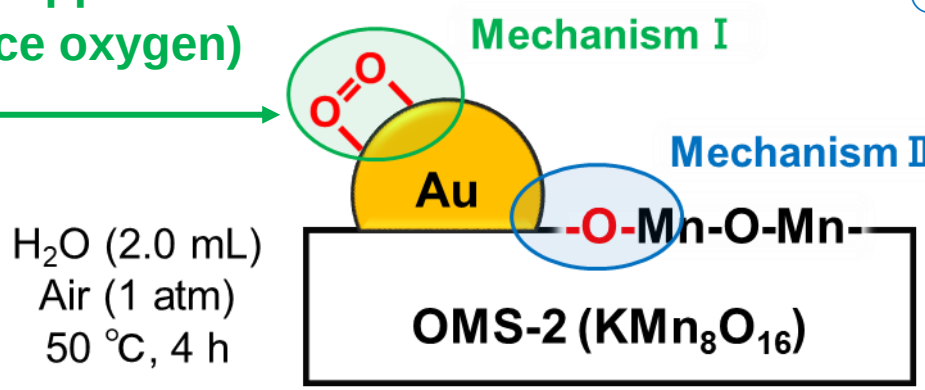


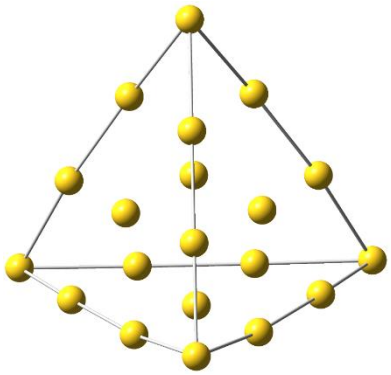
- The valence band of the Mn atoms were also shifted to the lower energy region in the $Au_{10}$/OMS-2 model.

○ With carbon support
(i.e., w/o lattice oxygen)

○ Under Ar atmosphere
(i.e., w/o gas-phase $O_2$)




**Lattice oxygens are not essential for the reaction.**



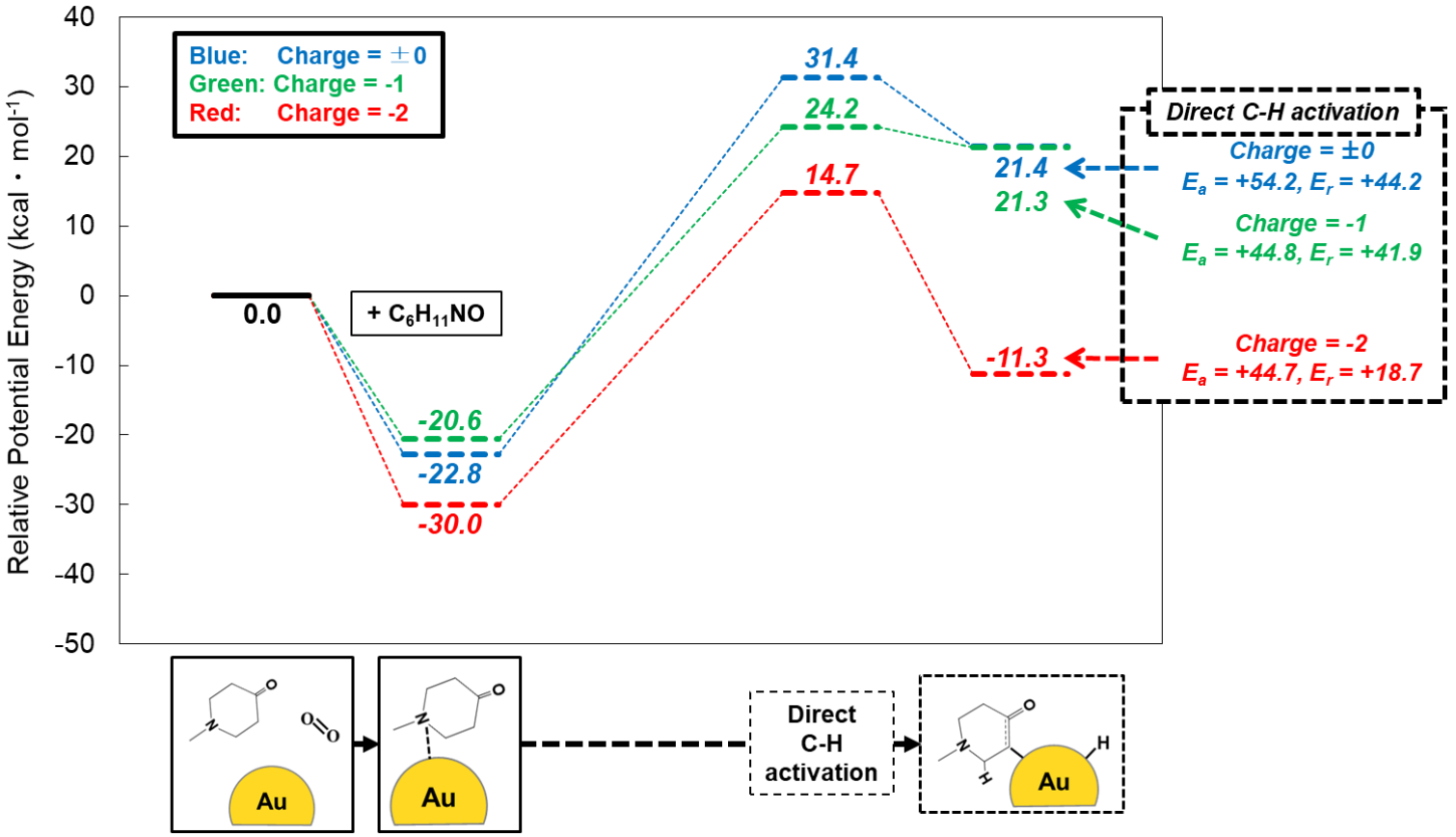
**$Au_{20}$ model**

**$Au_{20}$ model was adopted to investigate the reaction mechanisms.**
In addition, **total charge of the model system is set to ±0 or -1 or -2, respectively to investigate effect of the charge state of the Au cluster.**

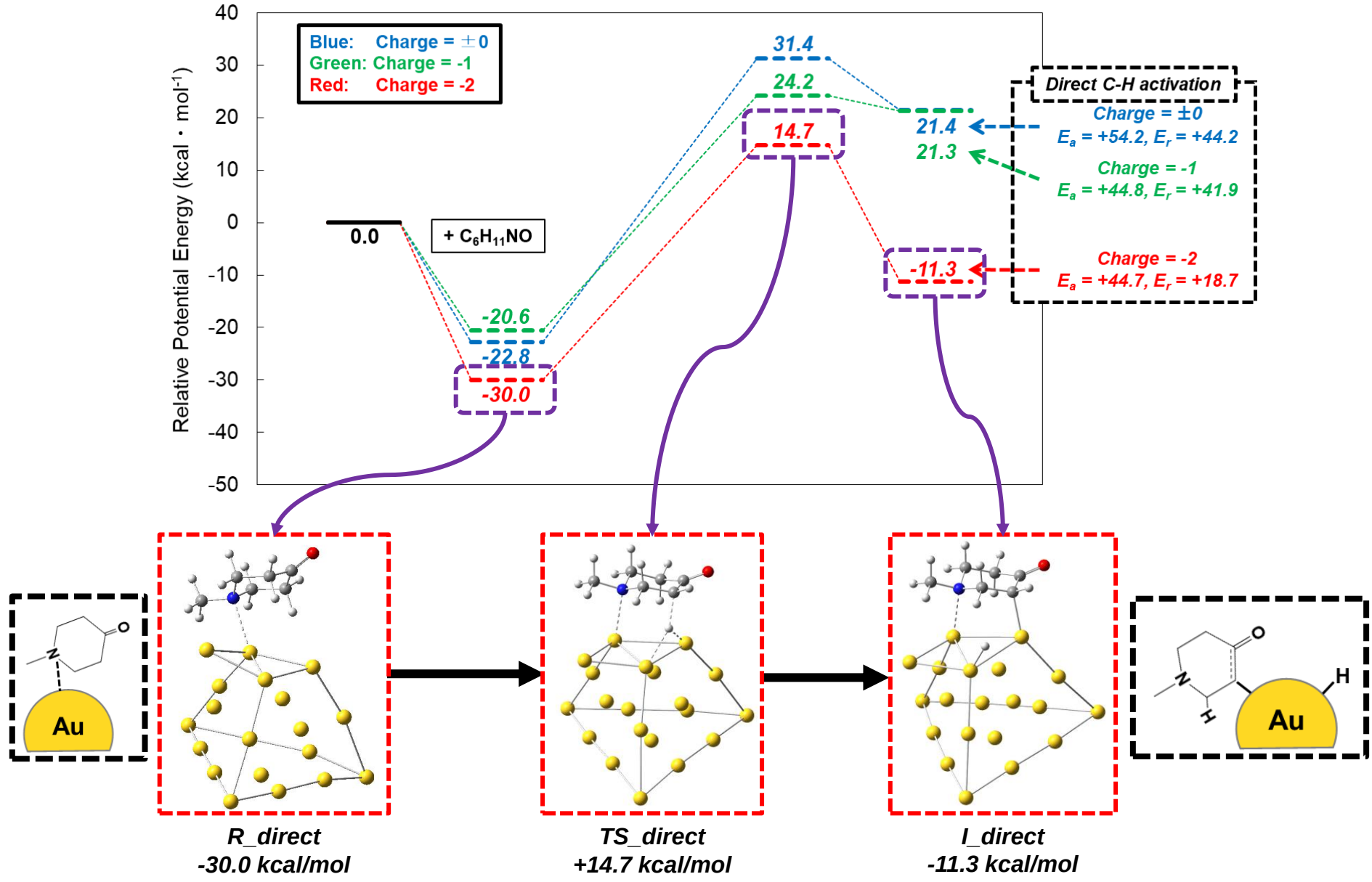
**Computational Details for the Cluster Model**

- Method : Density Functional Theory [DFT] (Functional : M06)
- Basis set : Au → Stuttgart/Dresden(611111/22111/411) ECP60MWB
  Other elements → 6-31G**
- Calculation Package: Gaussian09

First, **direct C-H activation pathways** on the $Au_{20}^{X}$ (x = 0, -1, -2) models were investigated.



First, **direct C-H activation pathways** on the $Au_{20}^{X}$ (x = 0, -1, -2) models were investigated.



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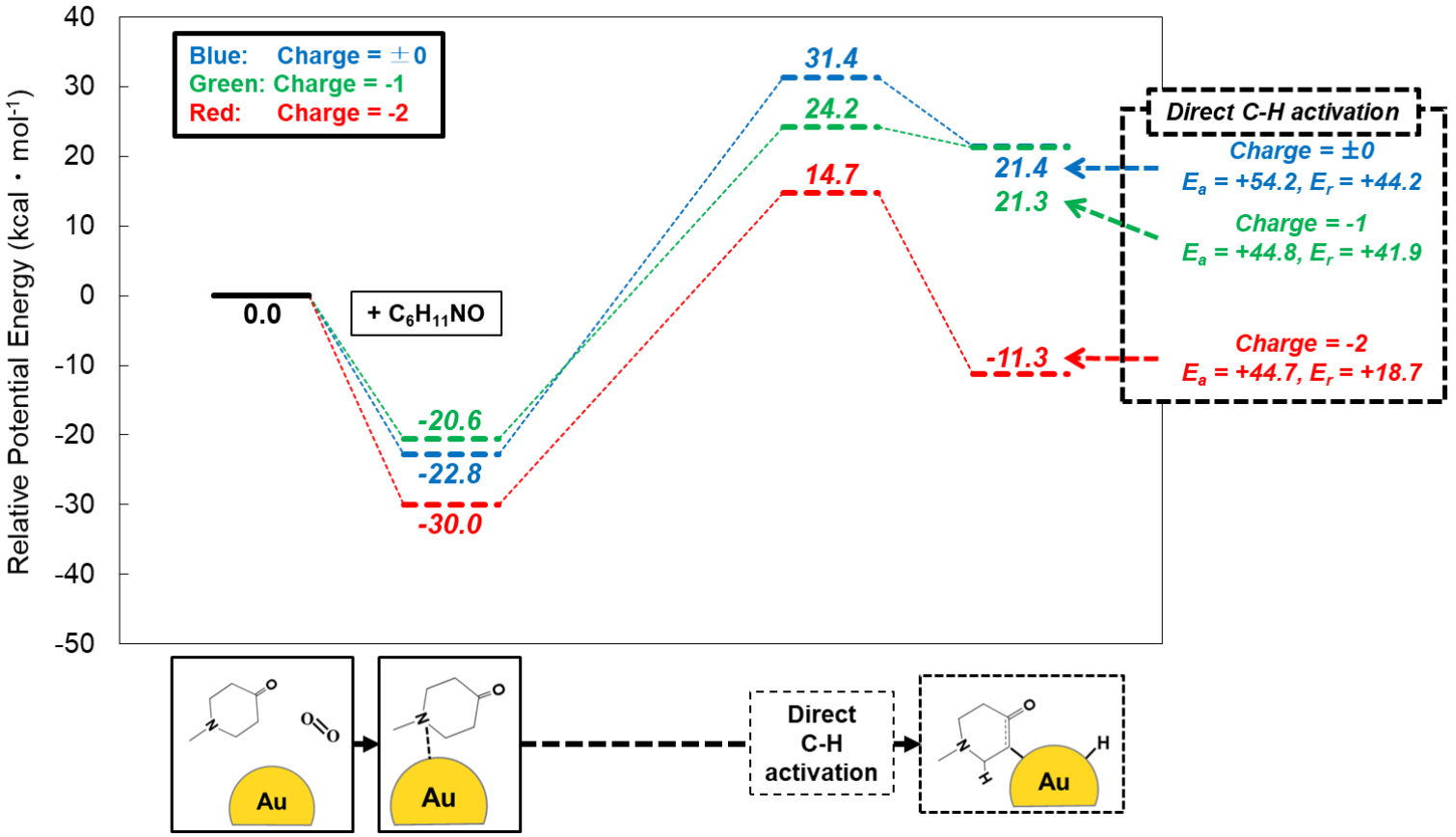
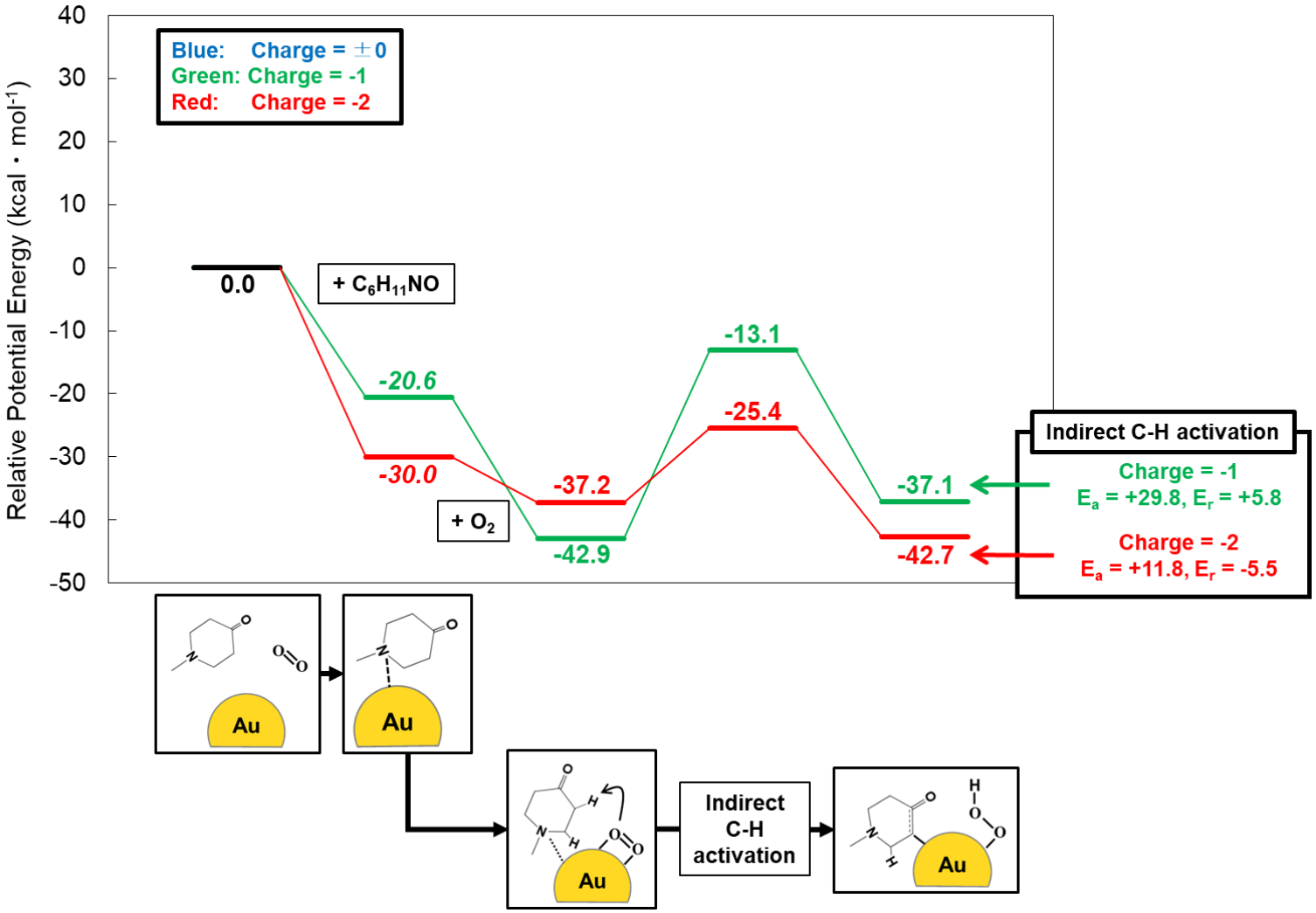



**Direct C-H activation takes place as endothermic reaction with high activation barriers in all models.**

**→The direct C-H activation on the Au/OMS-2 catalyst is unfavorable reaction pathway.**

Next, **$O_2$ supported indirect C-H activation pathways** on the $Au_{20}^{X}$ (x = -1, -2) models were investigated.



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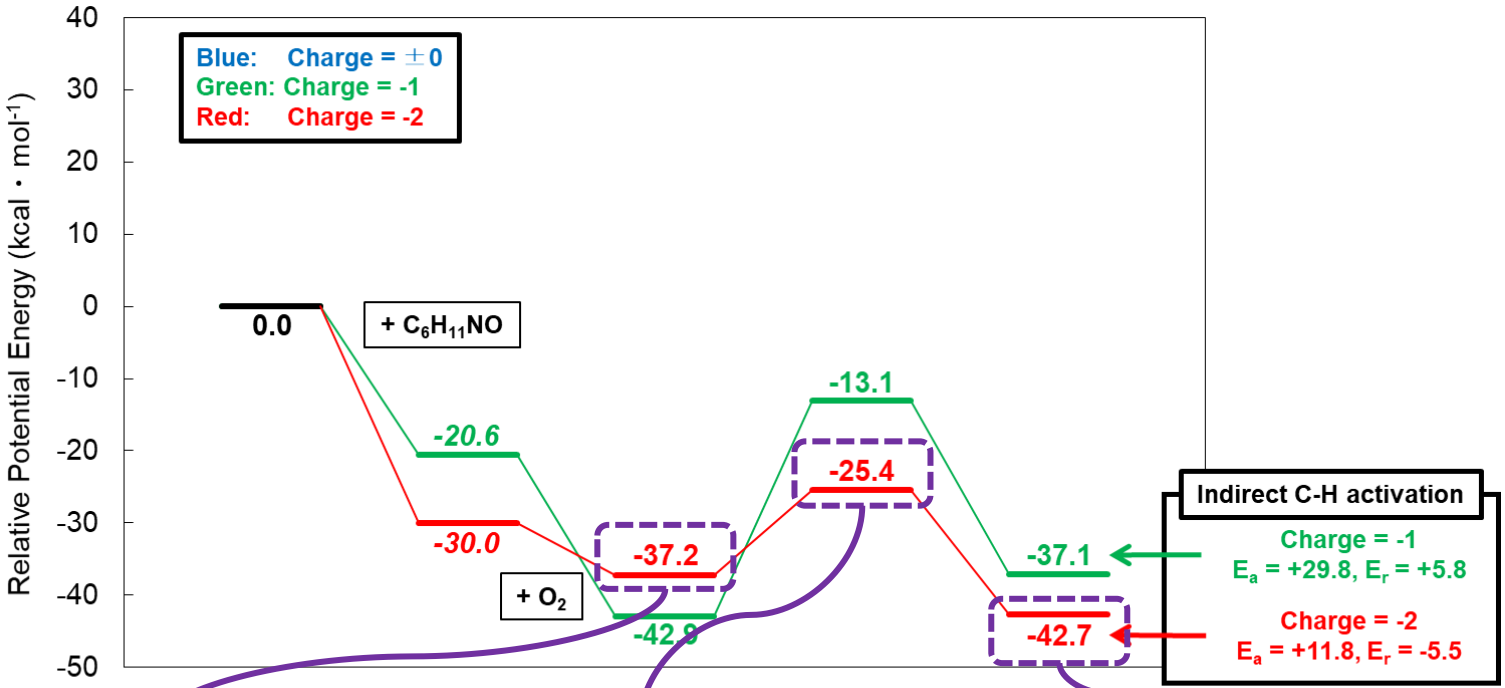
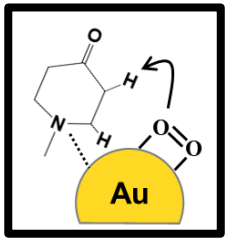
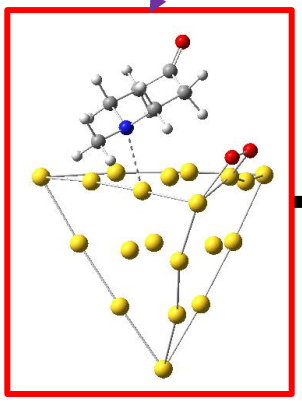
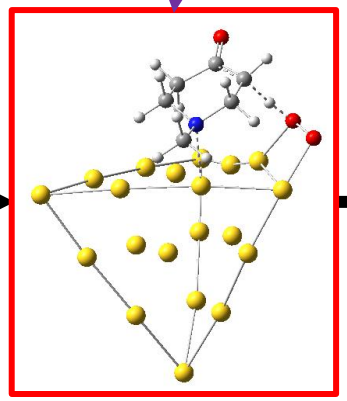


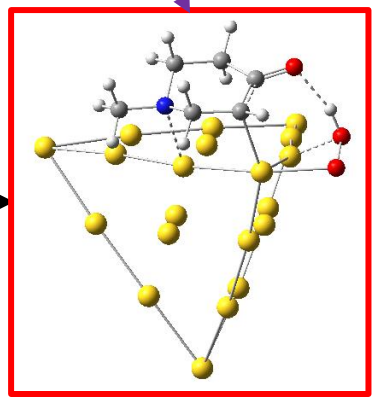



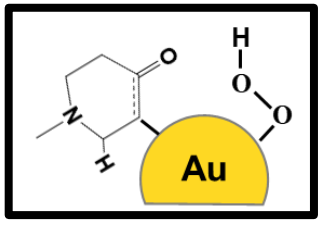
R_indirect
0.0 kcal/mol



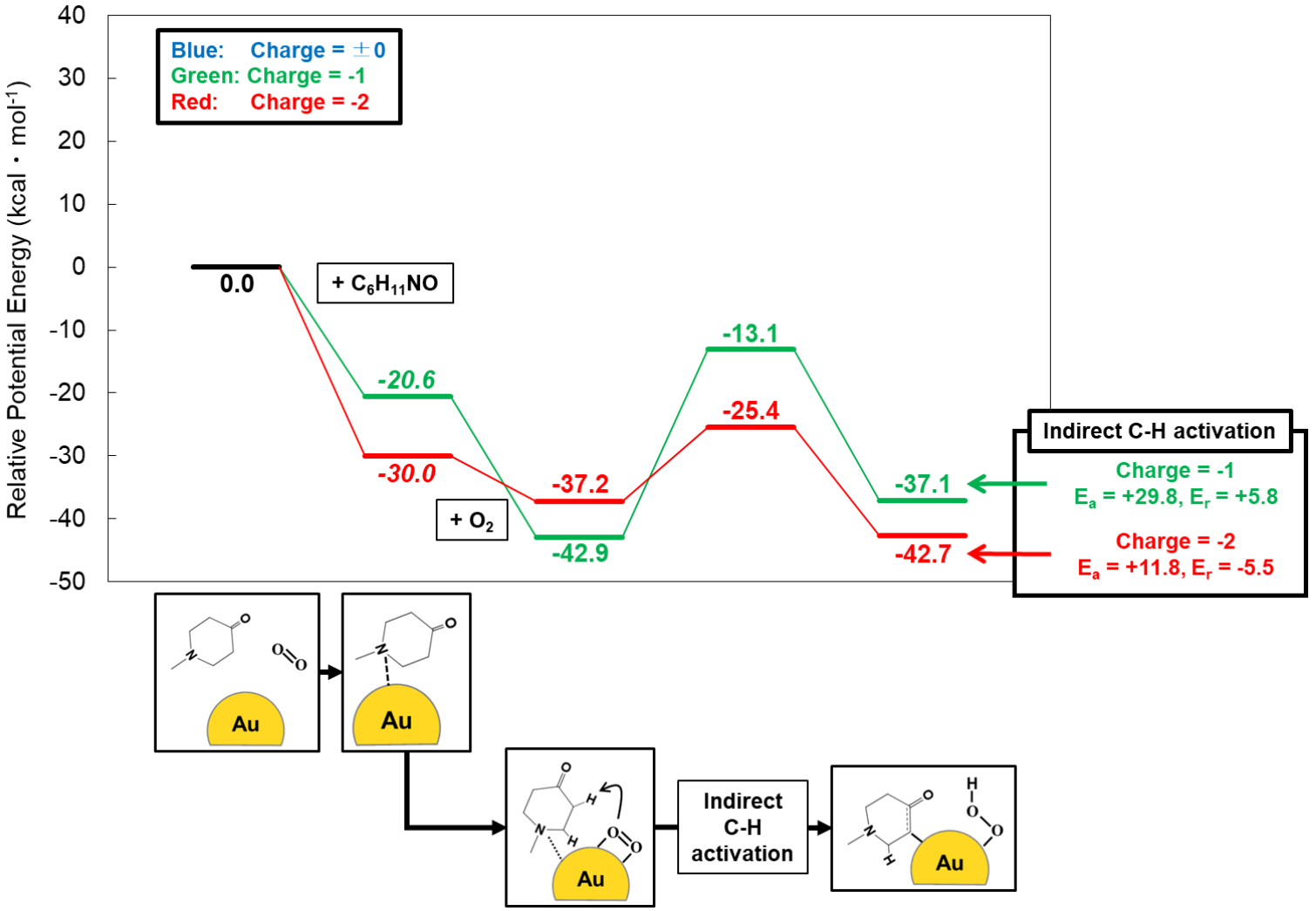
TS_indirect
+11.8 kcal/mol



I_indirect
-5.5 kcal/mol

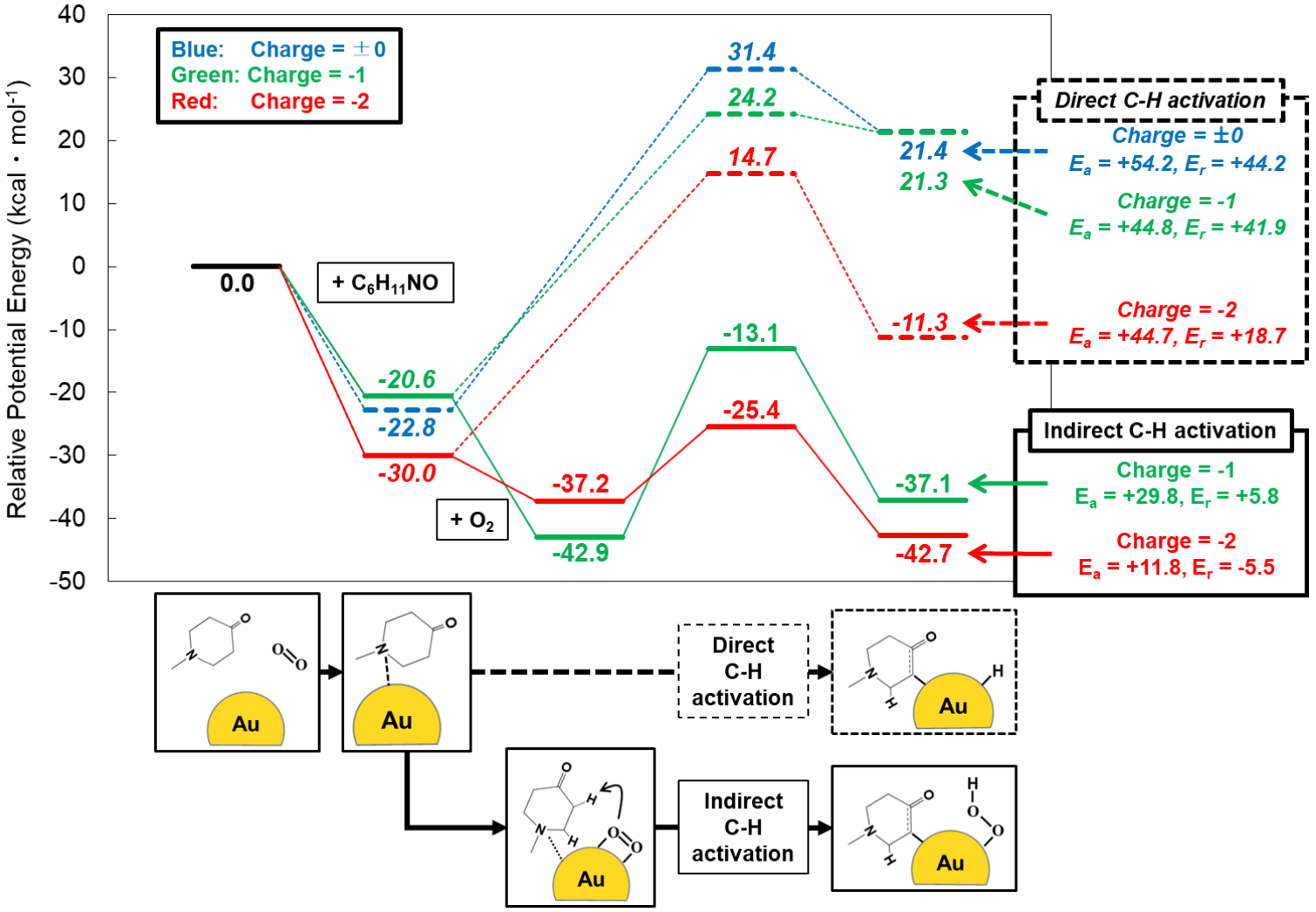


Next, **$O_2$ supported indirect C-H activation pathways** on the $Au_{20}^{X}$ (x = -1, -2) models were investigated.




**Activation energies of indirect C-H activation pathway on anionic $Au_{20}$ models are lower than that of direct C-H activation pathway by more than 15 kcal/mol.**

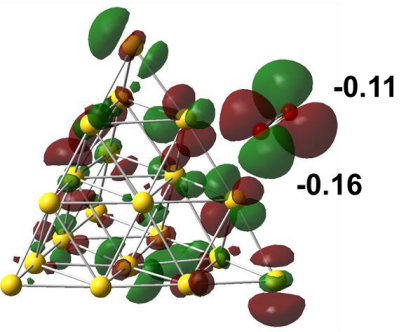
**Especially, indirect C-H activation pathway takes place as exothermic reaction on $Au_{20}^{2-}$ model.**




**From these results, indirect C-H activation pathway by adsorbed $O_2$ is reasonable reaction pathway of the Au/OMS-2 catalyst.**

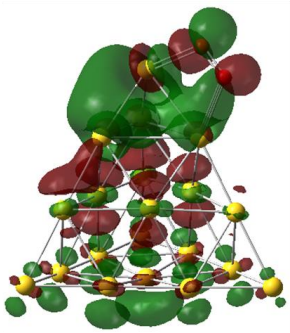
Next, electronic structures of adsorbed oxygen molecule were analyzed to investigate the reason why indirect C-H activation pathway is accelerated in the $Au_{20}^{2-}$ model.

Charge = ±0
Singlet
O-O = 1.25 Å

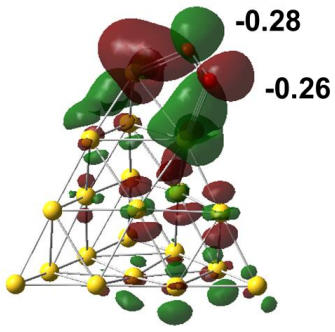



HOMO
-0.231

Charge = -1
Doublet
O-O = 1.30 Å

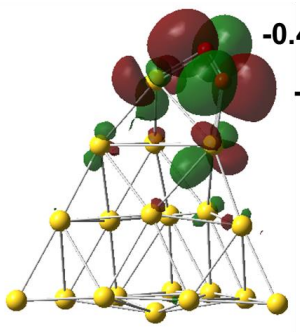


HOMO (α)
-0.128




HOMO (β)
-0.107

Charge = -2
Singlet
O-O = 1.40 Å



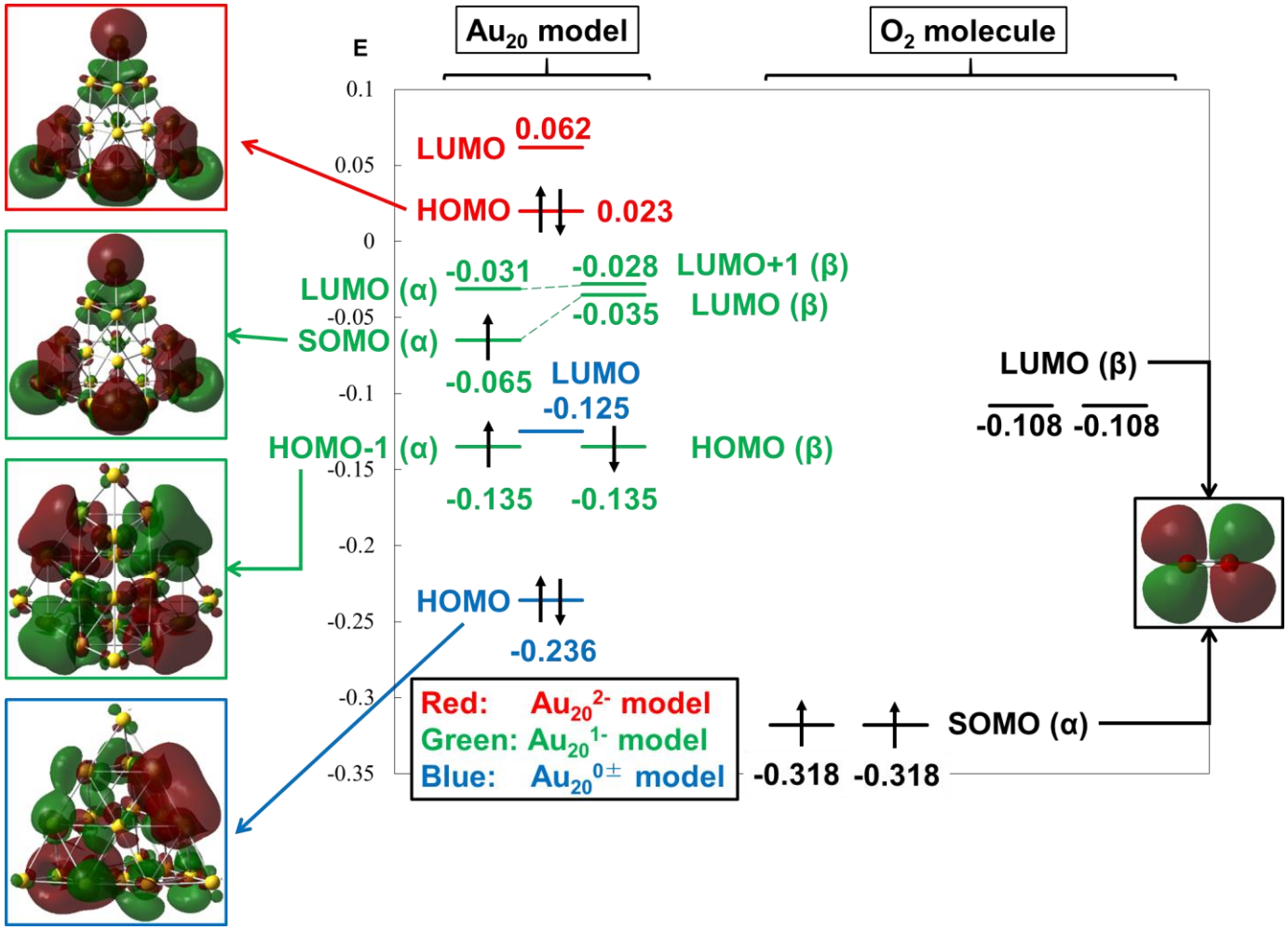

HOMO
+0.010

**Bond distance between oxygen atoms are increased in anionic $Au_{20}$ models.**

**Atomic charges of oxygen atoms become more negatively in negatively charged $Au_{20}$ models.**

**In addition, HOMO is localized on $\pi^*$ orbital of oxygen molecule in the $Au_{20}^{2-}$ system.**

**→Oxygen molecule is well activated on the negatively charged $Au_{20}$ models.**

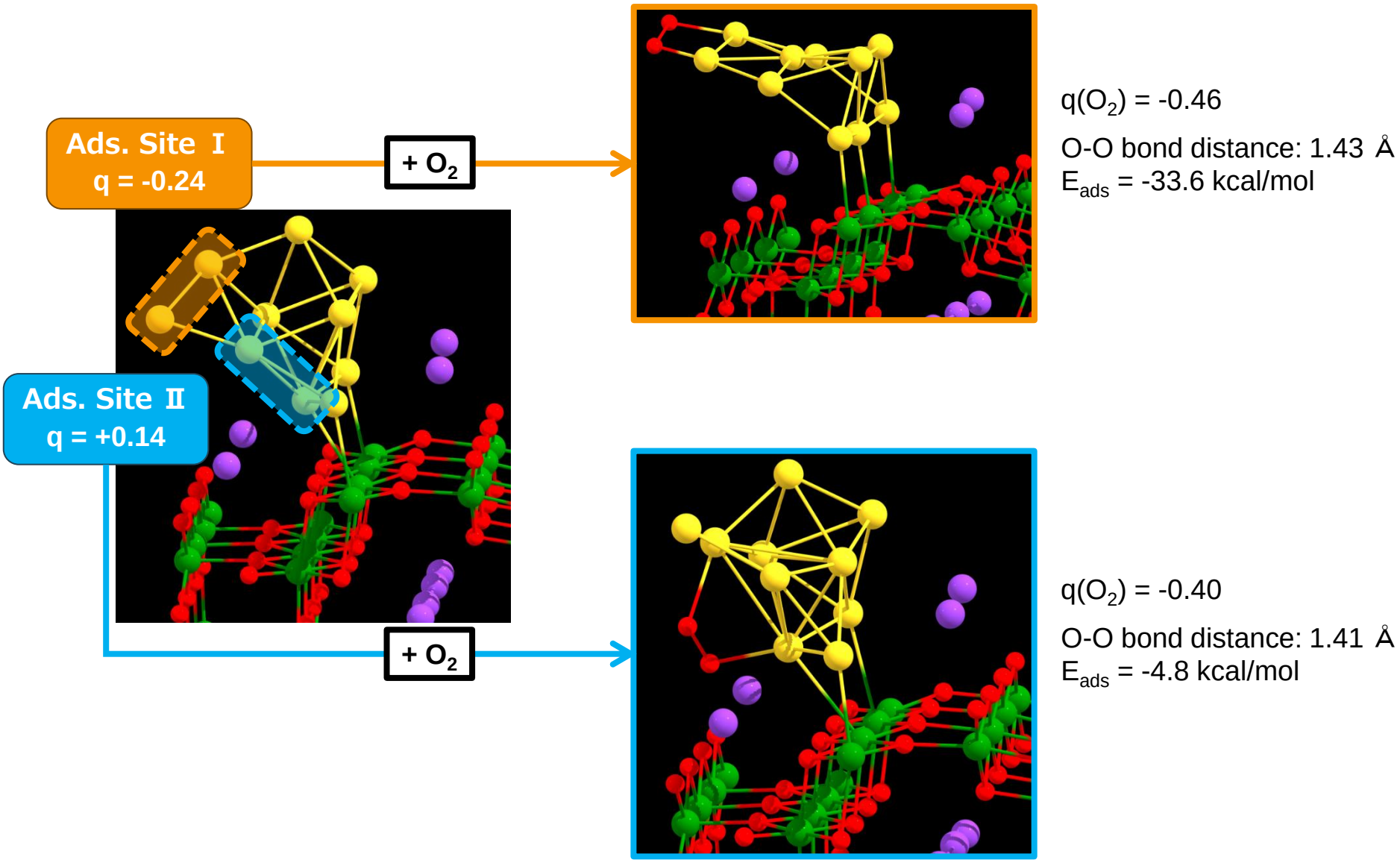



**HOMO level goes up in anionic charged $Au_{20}$ models.**

**HOMO level of negatively charged $Au_{20}$ models are higher than LUMO level of oxygen molecule.**

**→Charge transfer from the negatively charged $Au_{20}$ models to oxygen molecule is favorable.**

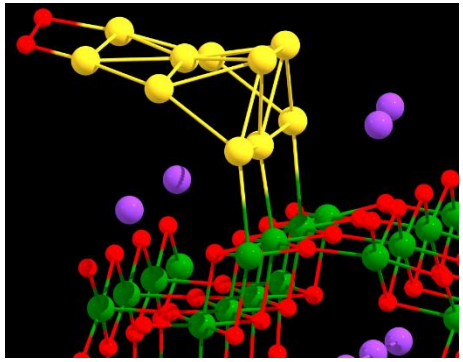
Electronic structure of adsorbed oxygen molecule on the $Au_{10}$/OMS-2 model was also investigated.




**$O_2$ is adsorbed on both sites stably, and O-O bond was elongated.**

**→$O_2$ is also activated on the $Au_{10}$/OMS-2 model.**

**$Au_{10}$/OMS-2 model + $O_2$**

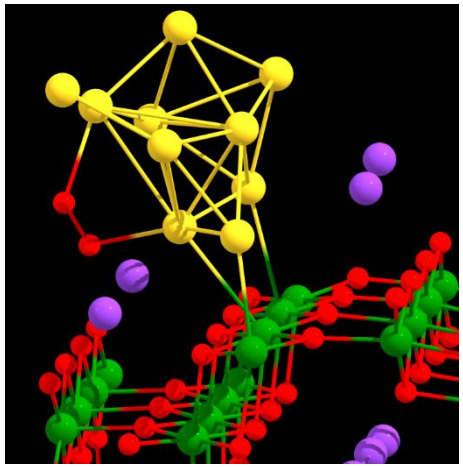


Ads. Site Ⅰ

$q(O_2)$ = -0.46

O-O dist.: 1.43 Å

$E_{ads}$ = -33.6 kcal/mol



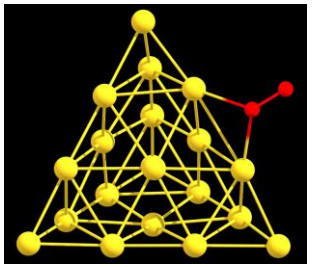
Ads. Site Ⅱ

$q(O_2)$ = -0.40

O-O dist.: 1.41 Å

$E_{ads}$ = -4.8 kcal/mol

**$Au_{20}$ model + $O_2$**

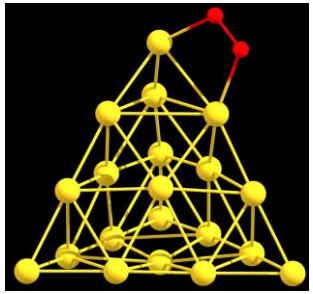


Total Charge = ±0

$q(O_2)$ = -0.24

O-O dist.: 1.29 Å

$E_{ads}$ = +18.9 kcal/mol

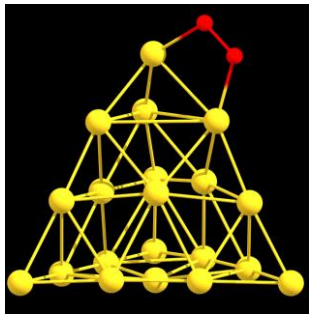


Total Charge = -1

$q(O_2)$ = -0.31

O-O dist.: 1.32 Å

$E_{ads}$ = -18.4 kcal/mol



Total Charge = -2

$q(O_2)$ = -0.51

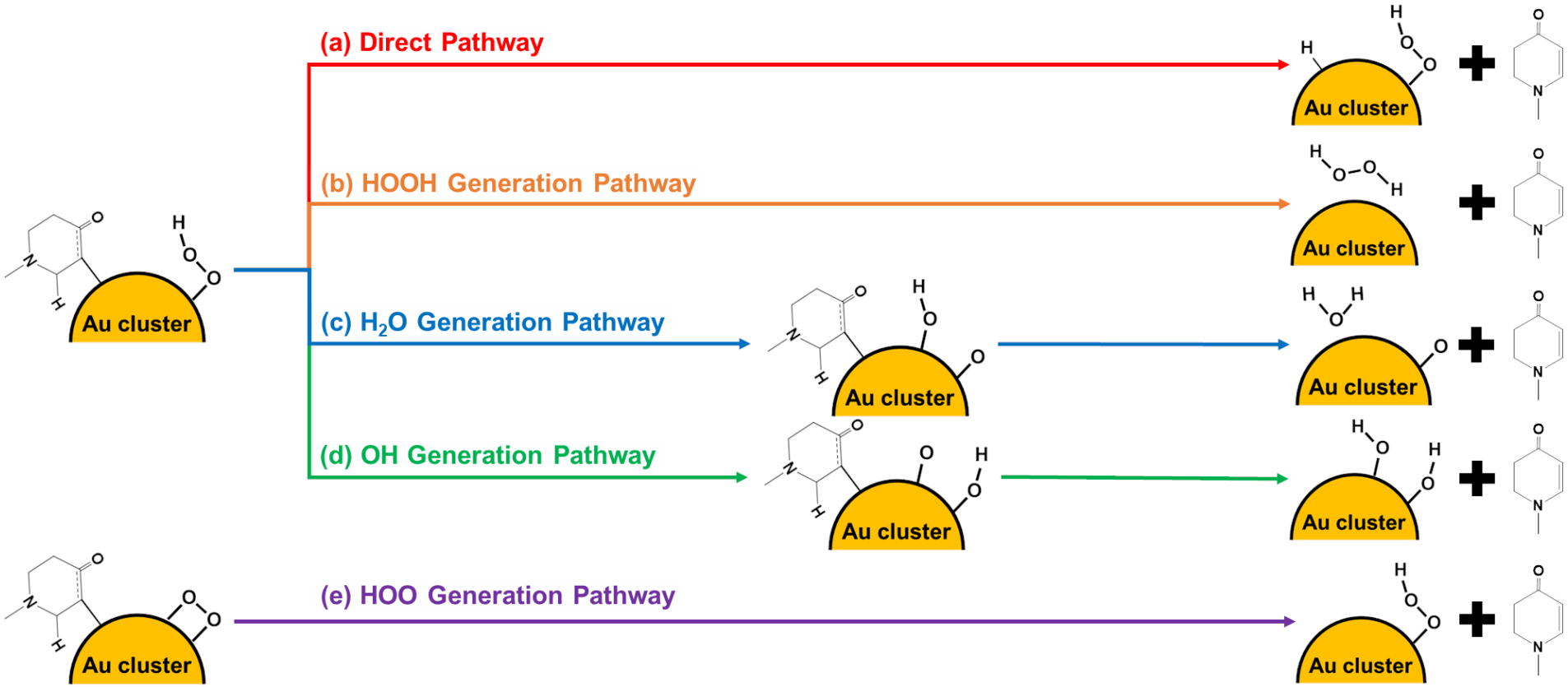
O-O dist.: 1.38 Å

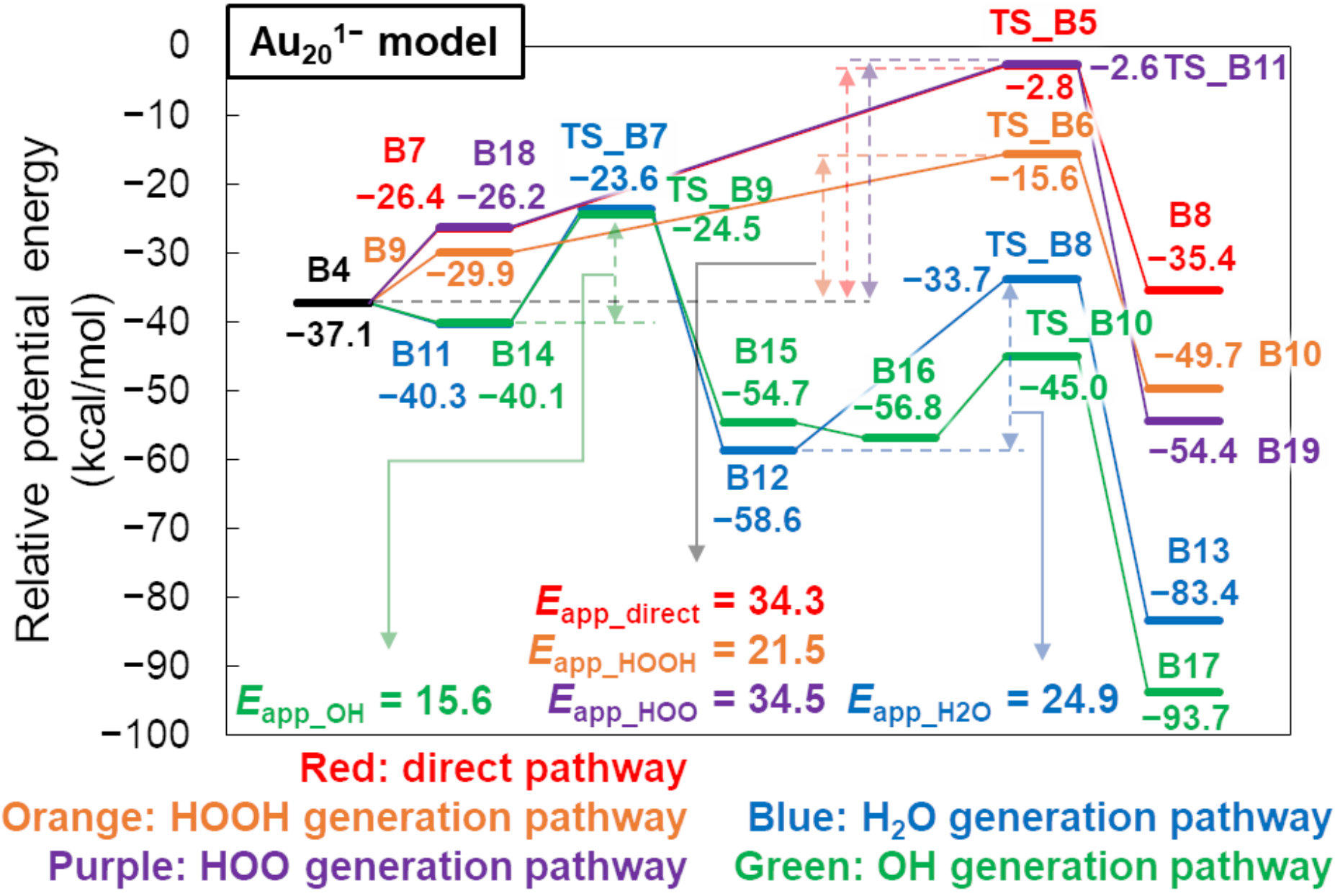
$E_{ads}$ = -23.7 kcal/mol

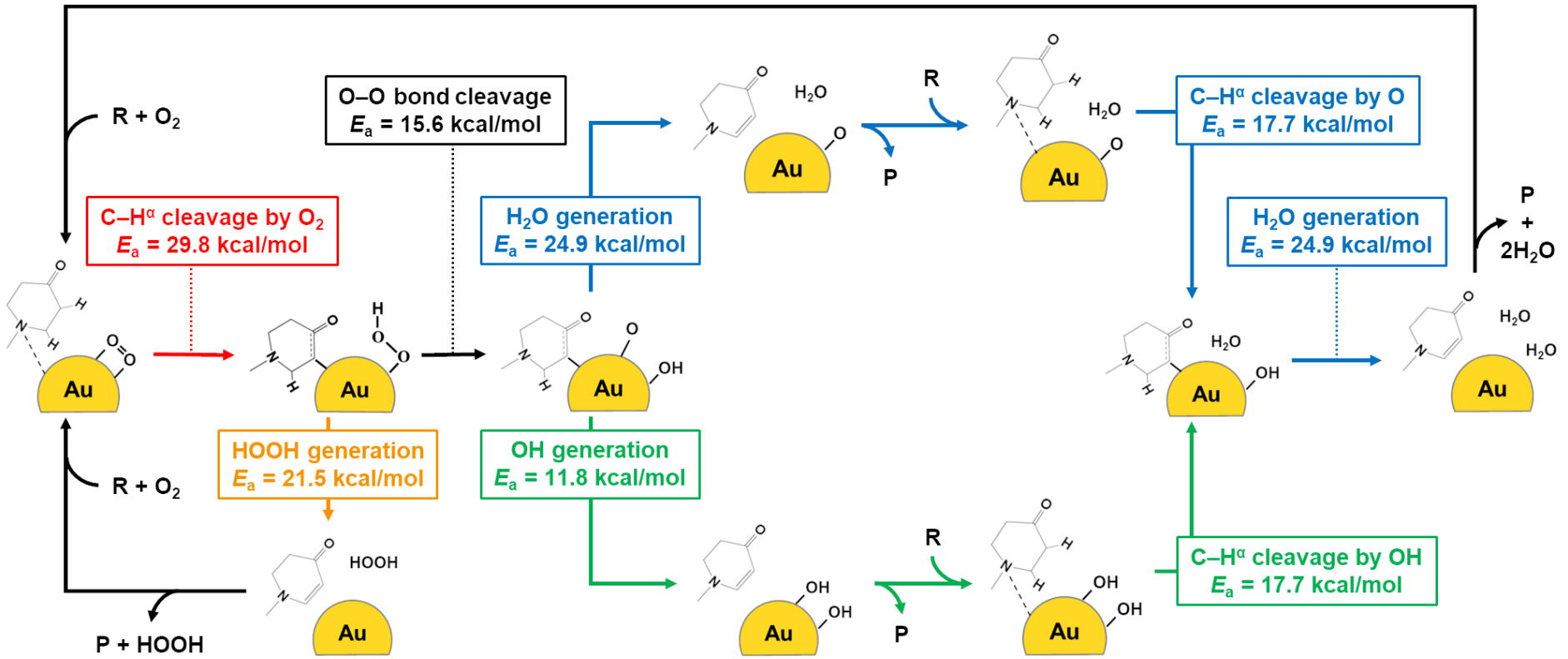
**Electronic structure of $O_2$ on the slab model is similar to that on the negatively charged cluster model.**

**→The effect of metal-support interaction is effectively included in negatively charged cluster models.**

There are five possible reaction pathways to activate the remaining C-Hβ bond.




Au20 1− model
Relative potential energy (kcal/mol)
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
B4
−37.1
B7
−26.4
B18
−26.2
B9
−29.9
TS_B7
−23.6
TS_B9
−24.5
B11
−40.3
B14
−40.1
B15
−54.7
B12
−58.6
TS_B5
−2.8
TS_B11
−2.6
TS_B6
−15.6
B8
−35.4
TS_B8
−33.7
TS_B10
−45.0
B16
−56.8
B10
−49.7
B19
−54.4
B13
−83.4
B17
−93.7
Eapp_direct = 34.3
Eapp_HOOH = 21.5
Eapp_OH = 15.6
Eapp_HOO = 34.5
Eapp_H2O = 24.9
Red: direct pathway
Orange: HOOH generation pathway
Blue: H2O generation pathway
Purple: HOO generation pathway
Green: OH generation pathway

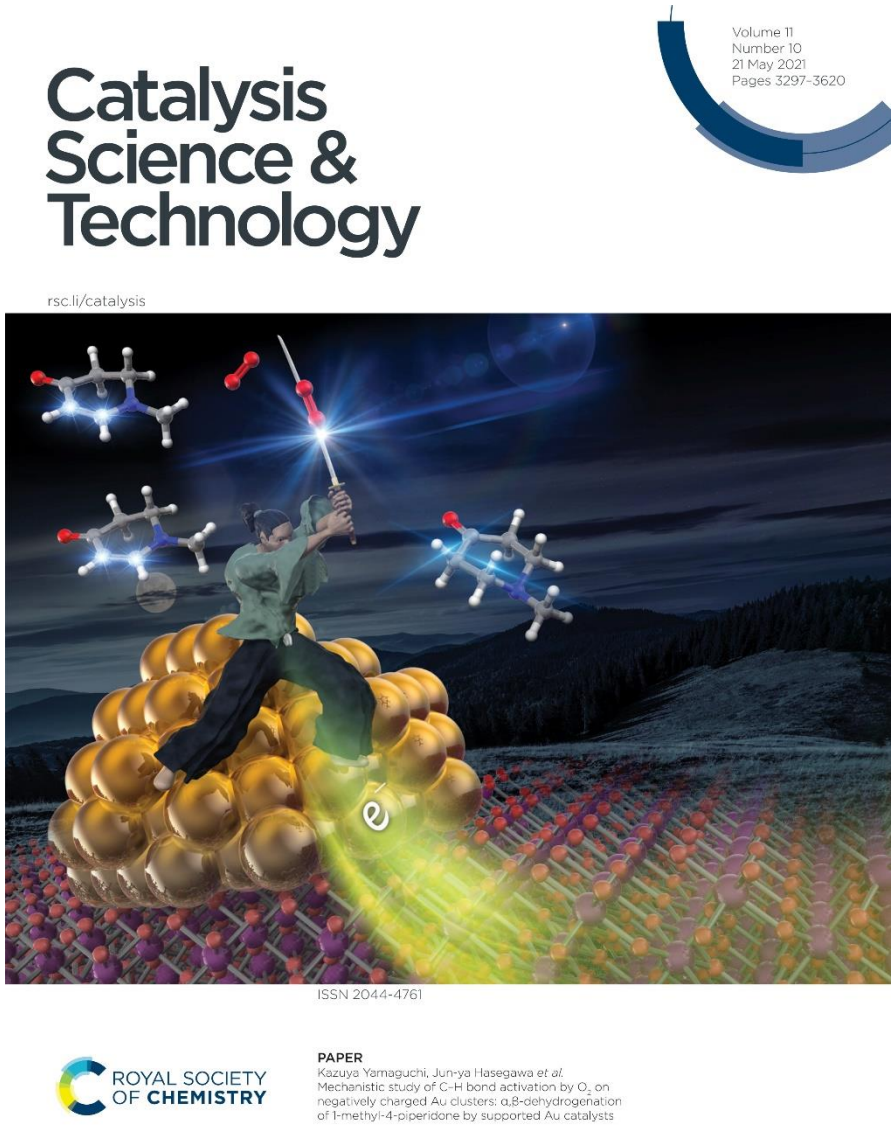

R + O2
C–Hα cleavage by O2
Ea = 29.8 kcal/mol
O–O bond cleavage
Ea = 15.6 kcal/mol
H2O generation
Ea = 24.9 kcal/mol
HOOH generation
Ea = 21.5 kcal/mol
OH generation
Ea = 11.8 kcal/mol
C–Hα cleavage by O
Ea = 17.7 kcal/mol
H2O generation
Ea = 24.9 kcal/mol
C–Hα cleavage by OH
Ea = 17.7 kcal/mol
R
P
P + 2H2O
P + HOOH
Au
OH
HOOH
H2O

- **Negatively charged Au cluster was formed via charge transfer from the OMS-2 support.**

- **Direct C-H activation pathway takes place as endothermic reaction with high activation energy.**

- **Indirect C-H activation by adsorbed $O_2$ takes place as exothermic reaction with low activation barrier.**

- **Not only the Au cluster but also the support material play important roles, and catalytic performance could be improved by designing the interaction between metals and supports.**




[1] **R. Miyazaki**, X. Jin, D. Yoshii, T. Yatabe, T. Yabe, N. Mizuno, K. Yamaguchi, J. Hasegawa, *Catal. Sci. Technol.*, 11, 3333-3346, (2021) [*Inside front cover*]

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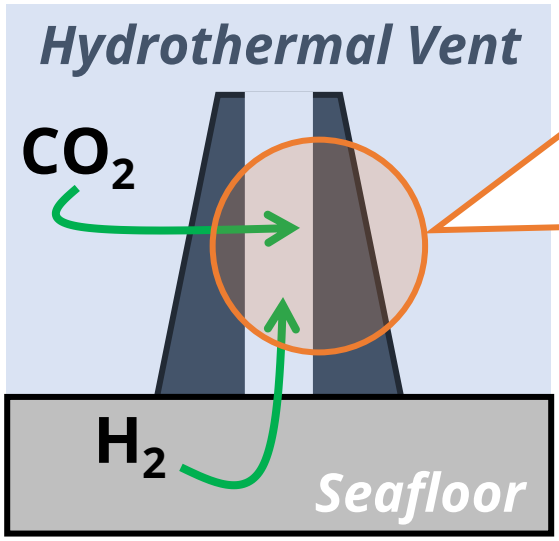
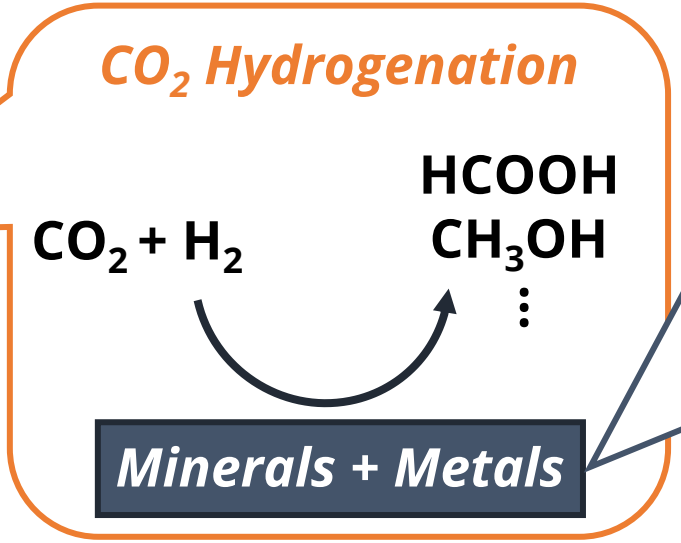
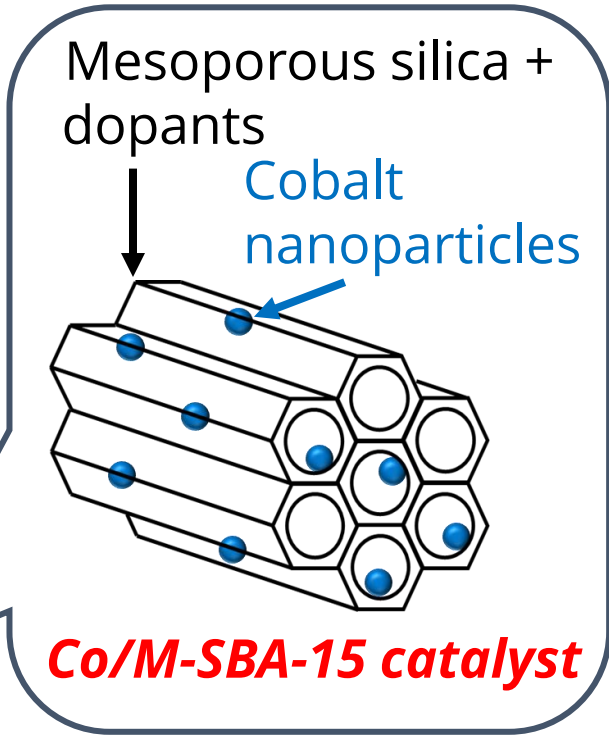
# *The FUNCAT Collaboration with MPI-KOFO*

(Kendra Belthle, Dr. Harun Tüysüz, Prof. Ferdi Schüth)




## SISSO

**Primary Features $\{x_n\}$**

- Experimental Data (by KOFO)
  (pore volume ($V$), particle size ($d$), …)
  +
- Theoretical Data (by FHI)
  (charge of cobalt($q$), adsorption energy ($E_{ads}$), …)

*Symbolic Regression* → **Descriptor Candidates**

$q * E_{ads}$
$d^3 - V$
⋮
$\{(V-d^3)^2 * q\}/(E_{ads})^3$
⋮

*Compressed Sensing*